CHEMICAL ENGINEERING SCIENCE
GENIE CHIMIQUE

VOL. 3 APRIL 1954 No. 2

The additivity of resistances in mass transfer between phases

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(*Received* 11 *November* 1953)

Summary—The concept of additivity of individual resistances to mass transfer between phases is confirmed by experimental measurements of transfer coefficients for vaporization of water into air, and the absorption from air of carbon dioxide, ammonia, and acetone by water.

Résumé—Les expériences de l'auteur vérifient la règle d'additivité des résistances individuelles aux échanges de matière entre phases.

Les coefficients d'échange ont été mesurés pour la vaporisation de l'eau dans l'air et pour l'absorption par l'eau de gaz carbonique, gaz ammoniac ou acétone mélangés à l'air.

The industrially important processes of gas absorption and liquid extraction involve mass transfer between two phases, and equipment design procedures commonly apply the well-known " two-film " or " two-resistance " theory [1], [2]. Although this practice has been general for many years there would appear to be inadequate experimental support for the concept of additive resistances, and it may be asked if, in fact, over-all coefficients can be calculated from values of the individual or " film " coefficients.

The usual theory assumes that there is no diffusional resistance of importance at the phase boundary, and the relationship between the concentrations of diffusing solute in the two phases at the interface is assumed to be the same as in static equilibrium measurements with bulk phases. Several investigators have suspected the existence of a diffusional resistance caused by the concentration of high-molecular weight solutes at the phase boundary, but such an effect has not been demonstrated in mass transfer tests where the interfacial area was fixed and definite. Even though there is no diffusional barrier at the interface, the relationship between the concentrations in the two phases at the interface may be expected to be different under conditions of dynamic equilibrium with diffusion than under the conditions of static equilibrium for which the equilibrium data are obtained. This effect, which might be expected to indicate an apparent interface resistance varying with diffusion rate, has been shown by SCHRAGE [3] to become important only at quite high rates of mass transfer, ordinarily attainable only at reduced pressures.

The additivity concept has been tested recently in liquid systems by GORDON and SHERWOOD [4], who also review the question of additivity of resistances in transfer between phases. A large number of solutes were transferred between water and iso-butanol in a stirred vessel, under conditions of known interfacial area. The measured values of the over-all coefficients were found to be well correlated using single values of the individual coefficients and the additivity concept. These results represent an excellent confirmation of the two-resistance theory, since the solutes used covered a 7,600-fold variation of the distribution coefficient. However, the values of the individual coefficients used in this correlation deviated 13 and 44 per cent, respectively, from the individual coefficients as measured directly by the extraction of iso-butanol into water and water into iso-butanol, with no third solute

present. This discrepancy was incompletely explained.

The present work is a study of the addivity principle in gas-liquid systems. Again a stirred vessel was used, with a constant known area of contact between phases. The tests involved the vaporization of water into air, the absorption of carbon dioxide, ammonia, and acetone from air by water, and the absorption of ammonia from air by aqueous solutions of sulphuric acid. The test of the additivity concept involved the comparison of the observed over-all coefficients for the absorption of ammonia and acetone with values predicted from the individual coefficients obtained from the experiments on water vaporization and carbon dioxide absorption.

Experimental Procedure

The thermostated cylindrical glass absorption vessel shown in Fig. 1 was used in all tests. It was 14·2 cm i.d. and 30·5 cm high. Air-gas mixtures were supplied to the upper gas space at constant condition and flow rate, but the liquid remained in place throughout each test. A down-flow propeller agitated the liquid ; the gas agitators consisted of the two flat-blade stirrers shown. Gas entering through a 14 mm o.d. glass tube was directed horizontally and tangentially to the blade tip of the lower gas stirrer, which barely cleared the end of this inlet tube. Calibrated glass thermometers were used in both gas and liquid. Laboratory compressed air was used as the carrier gas for the various solutes, the rate of flow being constant at 1,512 $\pm$ 20 l. per hour in all tests. The air was cleaned by being passed through a large bottle of glass wool and dried over calcium chloride. It was then metered, humidified by passing through a constant-temperature bubbler and a glass wool trap, preheated (or cooled) to the desired inlet test temperature, and passed to the absorption vessel. Heated air was used in the water vaporization tests ; in all other cases the inlet gas temperature was 25·07 $\pm$ 0·18°C. The liquid temperature was 24·95 $\pm$ 0·15°C. (In the sulphuric acid tests the liquid temperature rose from 25°C to about 26°C in the course of an experiment.) Test conditions (except liquid concentrations) remained exceedingly constant. The inlet and outlet gas streams were sampled by aspiration and both analyzed by appropriate techniques. Liquid samples withdrawn for analysis were replaced by equal volumes of distilled water.

In the case of the water-vaporization tests, the inlet air was preheated to a controlled dry-bulb

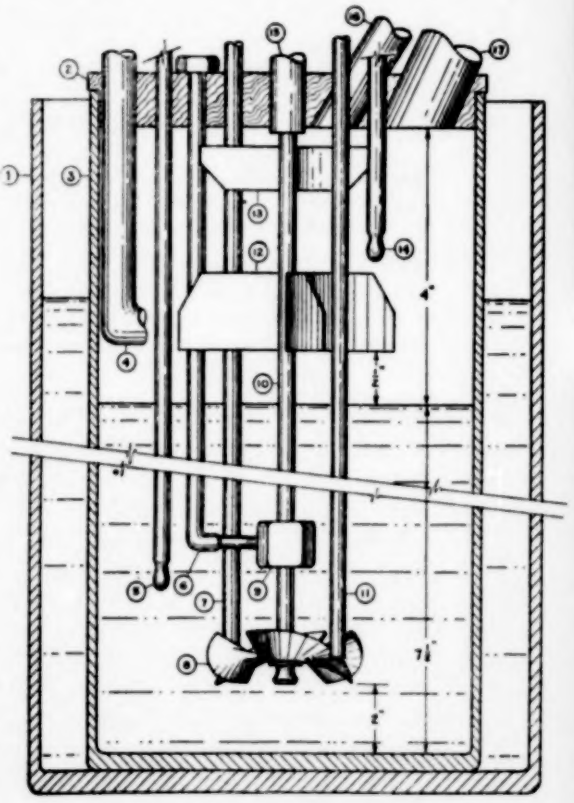

Fig. 1. Elevation of reaction vessel. 1, Thermostating bath; 2, vessel cover; 3, absorption vessel; 4, gas inlet tube; 5, liquid phase thermometer; 6, brace rod; 7, liquid replacement tube; 8, liquid phase stirrer; 9, supporting collar; 10, stirrer shaft; 11, liquid sampling tube; 12, lower gas phase stirrer; 13, upper gas phase stirrer; 14, gas phase thermometer; 15, mercury seal; 16, gas outlet tube; 17, access hole.

temperature (30 to 45°C) such that its wet-bulb temperature was 25°C. This was done in order that the temperature of the water surface would be essentially the same as the bulk liquid temperature, and permit the use of the latter in calculating the vapour pressure at the phase

boundary. In these tests the partial pressure of water in the inlet air was varied from 0·00745 to 0·02542 atm. in seven tests ; the partial pressure of water in the outlet air 0·0155 to 0·0272 atm. in the same series. Rate of vaporization was calculated from the air flow rate and the increase in partial pressure of water in the air. Air humidities were obtained gravimetrically by aspirating samples of some 16 l. of gas through drying tubes containing 'Anhydrone' (alumina was found to adsorb carbon dioxide from the air). Each test lasted approximately three hours ; data for only the middle third of the period were used. Explorations of the temperatures at some sixty points in a horizontal plane 13 mm above the liquid surface showed minor variations and a mean within 0·5° of the gas outlet temperature. It was concluded that the gas space was well stirred, and the outlet humidity was used in calculating the driving force for mass transfer.

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In the tests with carbon dioxide the inlet air, held at 25°C, contained 2 to 10·3 mole per cent carbon dioxide and was humidified to 98 per cent relative humidity to eliminate cooling of the water surface by vaporization. Tests varied in length from two to five hours. Carbon dioxide was supplied to the air stream after humidification from a pressure cylinder. Aspirated inlet and outlet gas samples were analyzed gravimetrically, using adsorption trains of ' Ascarite ' and ' Anhydrone ' in series. Only one inlet and one outlet gas sample were aspirated over the duration of each test. Because the rate of absorption was very low, the compositions of inlet and outlet gas streams were nearly identical. Rates of absorption were calculated from the liquid analyses, made by titrating 100 ml. samples taken at approximately 30 minute intervals. The carbon dioxide-water equilibrium data of MacInnes and Belcher [5] were used in calculating the over-all driving force from gas to bulk liquid.

The technique employed with ammonia was very similar to that for carbon dioxide. Both gas and liquid were at 25°, and the gas was nearly saturated with water. Inlet and outlet gas streams were analyzed for ammonia by titration following absorption of aspirated samples in bubbler tubes containing standardized hydrochloric acid. Gas concentration was varied from 0·3 to 1·1 mole per cent ammonia. Liquid samples were withdrawn into standard acid and back-titrated with standard sodium hydroxide. Gas samples were taken over approximately thirty-minute intervals. Liquid samples were withdrawn at the end of each of these periods. Partial pressures of ammonia over the week aqueous solutions encountered were taken from the correlations and data of Sherwood [6] and Breitenbach [7].

The procedure using acetone was also similar, except that acetone was not supplied from a cylinder, but from a thermostated acetone bubbler in the air feed line. Aspirated gas samples were drawn through bubblers containing distilled water. These solutions, as well as liquid samples from the absorption vessel, were analyzed by means of a Beckman spectrophotometer, Model DU, using a wavelength of 2,640 Å. This procedure, which was found to be simple and accurate in the range of 0·2 to 6 wt. per cent acetone, was checked against solutions of known concentrations.

Two tests were run in which ammonia was absorbed by aqueous solutions of sulphuric acid. The technique was essentially the same as for absorption of ammonia by water, except that the inlet air was humidified only to the extent of 95 to 99 per cent of the vapour pressure of water over the acid solution used.

Discussion of Results

The technique employed in studying the vaporization of water, whereby the wet-bulb temperature of the air over the liquid was adjusted to be the same as the water temperature, ensured the elimination of heat transfer into or out of the water, and made it possible to assume with confidence that the water surface temperature was the same as that of the bulk liquid. The mass transfer coefficients obtained in the vaporization of water into air, therefore, are individual values of k_G, not K_G. Carbon dioxide is sufficiently insoluble in water so that the gas side resistance calculated from the observed k_G for water vapour is less than 0·01 per cent of the over-all resistance. The observed coefficients for carbon dioxide,

therefore, are taken to be values of k_L rather than K_L.

Ammonia and acetone were chosen for the remaining tests, since their solubilities were such that calculations based on the observed values of k_G for water vapour and k_L for carbon dioxide indicated that for these gases, in the equipment employed, both gas and liquid resistances should be appreciable fractions of the total.

The experimental results are summarized in Table 1, which shows the observed values of K_G or K_L and outlet gas concentration in each test. Observed coefficients are seen to vary but slightly from the average in each series, though gas concentrations were varied appreciably. Liquid concentrations varied from zero to 17×10^{-4} g mole/l. for carbon dioxide, zero to 0·23 g mole/l. for ammonia, and zero to 0·11 g mole/l. for acetone. One acetone run was discarded, since the value of K_L was 12 per cent below the average for the other runs.

Table 1. *Summary of data**

Water Vaporization		*CO_2 Absorption*	
Outlet Partial Pressure, atm.	K_G	*Outlet Partial Pressure, atm.*	K_L
0·0232	0·212	0·0614	3·49
0·0198	0·200	0·0842	3·67
0·0155	0·192	0·1032	3·50
0·0166	0·204	0·1014	3·60
0·0272	0·194	0·0508	3·79
0·0200	0·204	0·0379	3·62
0·0251	0·212	0·0260	3·65
		0·0197	3·63
Ave.	0·203	Ave.	3·62
Range of vapour pressures – 0·03076 to 0·03098 atm.		Range of CO_2 concentrations in liquid – 0 to 0·0017 g moles/l.	
Ammonia Absorption		*Acetone Absorption*	
	K_L		K_L
0·0043	1·61	0·0150	1·92
0·0077	1·74	0·0122	1·93
0·0077	1·69	0·0095	1·97
0·0104	1·74	0·0075	1·93
0·0110	1·68	0·0059	1·91
0·0085	1·64	0·0025	1·94
0·0058	1·68		
0·0041	1·61	Ave.	1·93
0·0030	1·78		
0·0045	1·71		
0·0069	1·66		
Ave.	1·69		
Range of NH_3 concentrations in liquid – 0 to 0·23 g moles/l.		Range of acetone concentrations in liquid – 0 to 0·11 g moles/l.	

* The complete data may be obtained by writing to the second author. Copies of the twenty pages of original data will be supplied for the cost of reproduction.

The test of the concept of additive resistances consists in comparing the observed values of K_L for ammonia and acetone with the values calculated from the observed coefficients for water vapour and carbon dioxide. In making this comparison it is assumed that k_G is proportional to D_V^n and k_L proportional to D_L^m, where D_V and D_L are the molecular diffusivities in air and water, respectively. Fortunately, D_V for ammonia is very nearly the same as for water vapour, and D_L for ammonia is very close to the value for carbon dioxide. Consequently, the comparison of observed and calculated values of K_L for this solute depends very little on the assumed effects of diffusivities.

Many investigators in the field have employed the power function to represent the effect of diffuisvity, using values of n and m in the range of 0·15 to 0·67. Both exponents will be assumed to be 0·5, since this is not only representative of much of the experimental data, but is the value suggested by the penetration theories of HIGBIE [8] and of DANCKWERTS [9]. The addition of resistances then gives :

$$\left.\begin{aligned}\frac{1}{K_L} = &\frac{1}{H\,(k_G)_{H_2O}\left[\dfrac{D_V}{(D_V)_{H_2O}}\right]^{0.5}} \\ &+ \frac{1}{(k_L)_{CO_2}\left[\dfrac{D_L}{(D_L)_{CO_2}}\right]^{0.5}}\end{aligned}\right\} \qquad (1)$$

Using values of D_V and D_L for water, carbon dioxide and ammonia from PERRY [10], D_V for acetone from the GILLILAND [11] equation, and D_L for acetone from WILKE [12], the following ratios were obtained :

	Ammonia	*Acetone*
$D_V/(D_V)_{H_2O}$	0·921	0·367
$D_L/(D_L)_{CO_2}$	1·17	0·712

The comparison of observed and calculated coefficients is summarized in Table 2. Using the diffusivity ratios given above, the calculated value of K_L for ammonia is 1·76, which is to be compared with the observed value of 1·69. The calculated and observed coefficients for acetone are 1·89 and 1·93, respectively. The liquid side resistance is 45 per cent of the total in the case of ammonia, and 62 per cent for acetone. Thus the observed over-all coefficients agree within 3·5 per cent with the values calculated from the water and carbon dioxide data. The relative unimportance of the diffusivity correction in the case of ammonia is indicated by the fact that the predicted K_L is 1·73 when no diffusivity is made. The data lend excellent support to the concept of additivity of individual phase resistances, and suggest that over-all coefficients may be calculated with assurance from the individual coefficients. The concept of a substantial resistance at the interface appears to be incompatible with the data, except for the unlikely possibility that such a resistance, expressed in liquid-side concentration units, is the same for ammonia, carbon dioxide, and acetone, except as modified by the diffusivity correction.

Table 2. Summary of Results

	Experimental		*Calculated*	
	K_G	K_L	K_G	K_L
Vaporization of water	0·203	–	–	–
Absorption of CO_2	–	3·62	–	–
Absorption of NH_3 by water	–	1·69	–	1·76
Absorption of acetone by water	–	1·93	–	1·89
Absorption of NH_3 by acid (normality = 3)	0·182	–	0·192	–

The ammonia data give no insight into the effect of diffusivities since the ratios are so near unity. For acetone, however, the effect of the lower values of D_L and D_V should be significant. Assuming n and m equal, it is found that the observed and calculated values of K_L agree if these exponents are taken as 0·47. This is very close to the value 0·50 so commonly used in the literature.

Absorption in Acid

The absorption of ammonia by acid solutions should presumably follow the HATTA theory [2], with K_G increasing as the acid strength is increased until K_G becomes equal to k_G and then remaining constant as acid normality is increased above some critical value. The data of FELLINGER [13] show an anomaly in this connection, however, since K_Ga for the absorption of ammonia from air by sulphuric acid in a packed tower was found to increase steadily with acid strength up to 10N, and reach values more than twice as great as the apparent k_Ga as calculated from the K_Ga for ammonia absorption in water by allowing for the relatively small liquid-side resistance. In order to explore this point, two tests were run in which aqueous sulphuric acid was used for the absorption of ammonia.

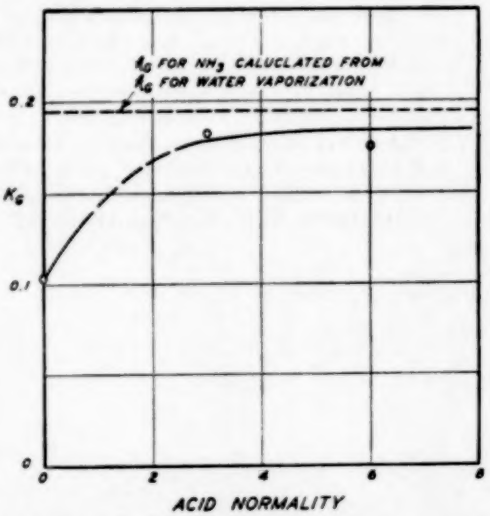

Fig. 2. Absorption of ammonia from air by water and aqueous solutions of sulphuric acid.

The results are shown in Fig. 2, with K_G plotted vs. acid normality. Although the data are incomplete, they fit well qualitatively with the Hatta theory. The over-all coefficient K_G increases with acid normality, reaching an apparent asymptote of about 0·182, which is not far from the value of 0·192 calculated from the value of 0·203 for water, with allowance for diffusivity based on the square root relation. The results do not support the anomaly suggested by the Fellinger packed tower data, which was possibly due to the equivalent of a variation of a with acid normality.

NOTATION

k_G = gas-side coefficient, g moles/(hr) (cm²) (atm).
K_G = overall-coefficient, g moles/(hr) (cm²) (atm).
k_L = liquid-side coefficient, cm/hr.
K_L = over-all coefficient, cm/hr.
D_L = molecular diffusivity in liquid, cm²/hr.
D_V = molecular diffusivity in gas, cm²/hr.
H = Henry's law constant, atm/(g moles/l).

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Chemical Engineering Science, 1954, Vol. 3, pp. 43 to 47. Pergamon Press Ltd.

Hydroextraction VIII : Cake formation

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(*Received* 27 *July* 1952)

Summary—It has been demonstrated that the mechanism of cake formation in a hydroextractor may be altered fundamentally by different methods of feeding the slurry to the basket. Examples are given of cakes growing in a direction parallel to the basket wall rather than normal to the wall, leading to the formation of wedge-shaped cakes.

Résumé—Etude théorique et expérimentale de l'écoulement au travers d'un gateau en forme de coin, aussi bien pour l'essorage. L'auteur compare l'equation précise de rélaxation à des relations simplifiées (écoulement du liquide uniquement dan la direction du champ de forces). Discussion d'une equation basée sur l'emploi d'une épaisseur uniforme, équivalente à l'épaisseur moyenne du coin.

Attempts to formulate equations representing the formation of hydroextractor cakes will depend on the mechanism controlled by the operating conditions and characteristics of the packing material. A cake may be formed with varying thickness by spraying slurry on to a cake fed with filtrate at less than the critical wetting rate [1], the solid remaining where it first hits the cake. Cakes of fine materials formed while submerged beneath a slurry layer may become either a wedge shape or a cake of nearly uniform thickness, depending on the characteristics of the material and the feed arrangement. Ideally, a slurry fed uniformly to the face of a hydroextractor basket builds a cake of uniformly increasing thickness at all heights on the basket wall. With a feed to the bottom of the basket various materials are found to build preferentially from the base of the cake and unless remoulded the final cake is wedge-shaped [5].

The final wedge shape is not necessarily produced by proportional growth over the whole surface of the cake. The cake may be formed predominantly from the bottom, the upward growth giving a thinner cake near the top. Thus the following limiting mechanisms could be formulated mathematically and compared with experimental facts :

(a) a cylindrical cake grows evenly at all positions,

(b) the cake grows upwards between two specified radii.

Case with Radial Growth of Cake

As one limiting mechanism consider the formation of a cake submerged beneath a slurry layer, i.e. $r_L < r_c$. Assume that the slurry is fed to a horizontal basket at a rate to maintain r_L constant, and that the cake grows evenly at all positions with equal increments of thickness. If the formation is begun on a cylindrical face, either of cloth or of cake material, the cake face remains vertical and cylindrical.

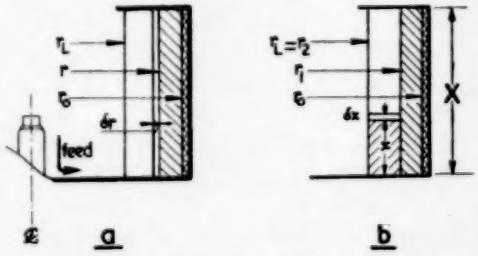

Fig. 1. Hypothetical types of growth for derivation of equations (5) and (10).

When an aqueous slurry of concentration s is fed to a hydroextractor basket spinning at n and the cake grows towards the axis of basket, keeping a smooth cylindrical surface (Fig. 1a), the cake surface radius r_c is related to the volume V of the slurry added from the start of formation :

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$$r_c^2 = r_0^2 - \frac{sV}{\pi \cdot X \cdot \sigma_P} = r_0^2 - C_1 V \qquad (1)$$

where $C_1 = s/\pi X \sigma_P$.
The rate of feed of slurry, q_s, and the rate of drainage of liquid through the cake, q_L, are related by :

$$q_L = \left(1 - \frac{s}{\sigma}\right) q_s \qquad (2)$$

It has been shown [1], [2] that for a liquid layer from r_L to r_c on a cake running full of liquid from r_c to r_0 :

$$q_L = \frac{4\pi^3 n^2 KX (r_0^2 - r_L^2)}{\mu g \log_e \frac{r_0}{r_c}} \qquad (3)$$

This equation was appropriate to the cakes tested as the sedimentation rate in the nominal slurry layer from r_L to r_0 was so high that the layer was effectively liquid only.

When a layer of thickness $(r_0 - r_c)$ and permeability K is formed on an initial layer of thickness $(r_w - r_0)$ and permeability K_0, the flow rate of liquid through the banded cake is

$$q_L = \frac{4\pi^3 n^2 X}{\mu g} (r_c^2 - r_L^2) \times \left[\frac{1}{K} \log_e \frac{r_0}{r_c} + \frac{1}{K_0} \cdot \log_e \frac{r_w}{r_0}\right]^{-1} \qquad (3a)$$

when forming cakes on highly permeable cloth K_c may be fifty times K and with $(r_w - r_0) = (r_0 - r_c)$ the second term in the bracket is 2% of the first term and thus the cloth term soon becomes of minor importance when building a thick cake. It is questionable, however, whether this type of equation is valid once the low permeability layer is appreciable, as the highly permeable cloth will probably cease to run full of liquid, and atmospheric pressure is transmitted to the radius r_0 [4]. In view of the short time required to reach this stage, the equation (3) has been used, which accords with the assumption of a large value for K_0 in equation (3a). Thus

$$q_s = \frac{CX}{\log_e \frac{r_0}{r_c}}, \quad \text{where } C = \frac{4\pi^3 n^2 K (r_0^2 - r_L^2)}{\mu g \cdot \left(1 - \frac{s}{\sigma}\right)}$$

$$\frac{dV}{dT} = \frac{CX}{\log_e \left(\frac{r_0}{(r_0^2 - C_1 V)^{\frac{1}{2}}}\right)} \qquad (4)$$

When integrated from $V = 0$ at $t = 0$ to $V = V$ at $t = t$, assuming C and C_1 to be constant, equation (4) becomes :

$$(1 + 2 \log_e r_0) V + \left(\frac{r_0^2}{C_1} - V\right) \times \log_e (r_0^2 - C_1 V) - \frac{2r_0^2}{C_1} \log_e r_0 = 2CXT \qquad (5)$$

Case with Upward Growth of Cake

If the cake is assumed to grow in a direction parallel to the axis of rotation and confined between radii r_1 and r_2 (Fig. 1b), the relation between r_1, r_2 and V is given by

$$\frac{sV}{\sigma_P} = \pi x (r_0^2 - r_L^2) \qquad (6)$$

$$\text{or } x = C_2 V, \text{ where } C_2 = \frac{s}{\pi \sigma_P (r_1^2 - r_2^2)}$$

Assuming that this cake is being formed on an existing cylindrical layer of inner radius r_1 and the same permeability K,

$$q_s = \frac{4\pi^3 n^2 K (r_0^2 - r_L^2)}{\mu g \cdot \left(1 - \frac{s}{\sigma}\right)} \left[\frac{x}{\log_e \frac{r_0}{r_2}} + \frac{X - x}{\log_e \frac{r_0}{r_1}}\right] \qquad (7)$$

whence

$$\frac{dV}{dt} = C \left[\frac{C_2 V}{\log_e \frac{r_0}{r_2}} + \frac{X - C_2 V}{\log_e \frac{r_0}{r_1}}\right] \qquad (8)$$

$$= R_1 V + R_2, \text{ where } R_1 = CC_2 \left[\frac{1}{\log_e \frac{r_0}{r_2}} - \frac{1}{\log_e \frac{r_0}{r_1}}\right]$$

$$R_2 = \frac{CX}{\log_e \frac{r_0}{r_1}}$$

From integration with $V = 0$ at $t = t$, assuming R_1 and R_2 to be constant,

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$$e^{R_1 t} = 1 + \frac{R_1}{R_2} \cdot V \tag{9}$$

or
$$t = \frac{1}{R_1} \cdot \log_e \left(1 + \frac{R_1}{R_2} \cdot V\right) \tag{10}$$

The significance of the equation is limited to the range $0 < x < X$.

Fig. 2 is a comparison between the theoretical equations (5) and (10) for the set of experimental

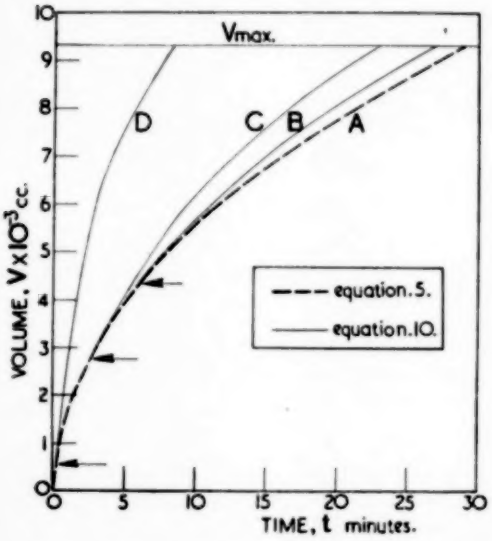

Fig. 2. Comparison between equations (5) and (10).

constants given in Table 1. The time required for forming a certain cake according to equation (10) is much less than that to be predicted from equation (5), especially when the building starts on a thin layer. The calculations required for the use of equation (5) are extensive and require seven figure accuracy.

Curve A is from equation (5) based on a negligibly small initial resistance. Curves B, C, D are from equation (10) representing different initial cake layers from r_1 to r_0. The meet of curves B and A represents the volume of slurry that formed the initial cylindrical layer, which could have been formed by the mechanism of equation (5), the formation following equation (10) thereafter.

Experimental Results

A twelve litre glass vessel was equipped with a mechanical agitator, a feeding tube to the floor of the basket and an inclined graduated tube from the side for measuring the level of the slurry in the vessel. Dilute starch slurries of selected concentration were used for the tests, as chalk cakes were found to crack occasionally under the test conditions.

The hydroextractor basket was fitted with two layers of cloth support of high permeability and run at a specified speed with water being fed to it to maintain the liquid inner radius constant at a selected value of r_L. This was done using the probe arrangement as an indicator for r_L [2], [3]. The slurry was then fed to the basket, starting at the moment when the water feed was stopped, and the rate continuously regulated to maintain r_L constant. The level on the calibrated side tube was recorded every 15 or 30 seconds according to the rate of feeding.

Concentrations of 0·10 to 0·20 g air-dried starch/cc slurry were used. Cake formation was studied by feeding slurry directly on to the cloth support or on to an existing cylindrical cake of smooth surface, and known dimensions and permeability. Tests were done at different speeds of rotation and different radii r_1 and r_L. Constant dimensions and cake characteristics appropriate to representative tests are quoted in Table 1.

The surfaces of the resultant cakes and of intermediate forms were traced using the probe. To give a clear visual indication of the way in which the cake grows, in some tests the addition of slurry was interrupted at intervals to feed a small amount of a solution of starch and iodine. After completing the formation, the cake was run dry for some minutes and then vertical sections cut from it and withdrawn from the basket. Fig. 3 shows sections of representative cakes along the plane of the axis of rotation, the contours of which were measured by the probe [2] for comparison with stained sections. It demonstrates that the cake formation starts with a wedge at the bottom of the basket. This increases in thickness up to the inner radius of the slurry r_L. At this stage, the wedge may be of more than an inch thick at the bottom with

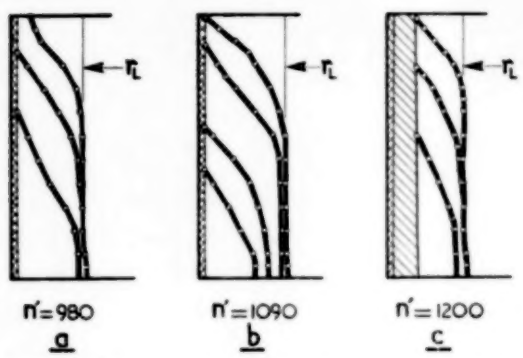

Fig. 3. Contours representing the growth of hydroextractor cakes.

zero thickness at the top of the basket. Thereafter the main growth of the cake is in a direction parallel to the axis of rotation, with hardly any increase in cake thickness at the bottom. This mechanism suggests that the experimental V, t data will not agree with the function given from equation (5). The data in Fig. 3 show a similar formation at different speeds of revolution, different positions of the liquid surface, and for formation on cloth (Figs. 3a, b) or on an existing cake of constant thickness (Fig. 3c).

Curve A in Fig. 4 is predicted from equation (5), curve B from equation (10) for the set of experimental results represented by the data, using the data in Table 1 representing the known geometry, and characteristics of the cake material. The set A, B is for a cake formed on an existing layer of starch, whereas the set of curves A′, B′ is for a cake formed directly on the cloth. If the cloth is assumed to have negligible resistance to flow, equation (10) becomes inapplicable. Hence curve B′ has been made to represent a cake which grew from an initially uniform thickness of one millimetre. This is expected to lead to a slightly higher time than the exact value that could be obtained from equation (10) alone taking the resistance of the cloth into consideration, if the cloth was assumed to remain full of liquid.

In both cases, the failure of equation (5) is clear, whereas equation (10) gives theoretical lines nearly coincident with the practical results. A variety of cases is represented in Fig. 5 where the agreement between the practical

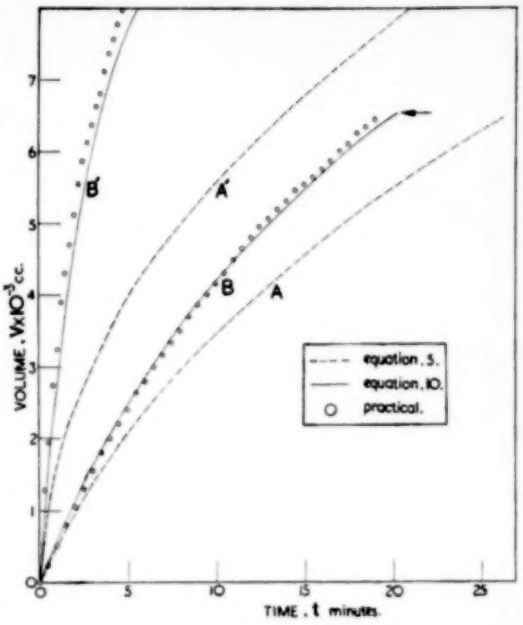

Fig. 4. Comparison of practical results with theoretical curves. The arrow indicates the volume of slurry equivalent to the cake volume to fill the basket.

results and predicted curves from equation (10) is confirmed. The relevant data for all the curves are presented in Table 1.

In the above calculations the overall mean permeability, including the effect of cloth-cake interface resistance [3], was considered constant, and taken as the permeability of a cake formed from half the material used in the test. The permeability actually increases from outer to inner layers of the cake [3] as well as from bottom to top of the basket.

Correction for the former type of variation will not produce a significant change in the deviation of equation (5) from the experimental data. In the case of equation (10), the latter variation in permeability would decrease the curvature of the predicted curve and make it more nearly coincident with the experimental data. However, this variation is of minor importance when testing starch as the porosity was nearly constant along the vertical direction through the hydroextractor cakes.

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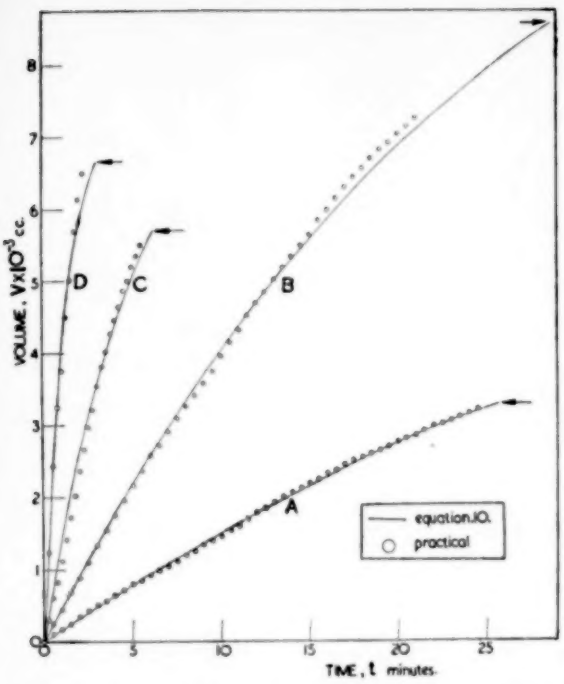

Fig. 5. Agreement between practical results and equation (10). The arrow indicates the volume of slurry equivalent to the cake volume to fill the basket.

Conclusions

Even with submerged cakes, formation may not be assumed to occur by growth all over the cake surface, when a dilute slurry is fed to the base of the basket. By assessing face contours during stages of the formation, an approximate equation may be derived from the hydroextraction equations, as in the cases described which conform closely to the upward growth mechanism. The appropriate equation depends on the materials used and the operating characteristics.

Table 1. *Test conditions and cake characteristics*

$\sigma_P = 0{\cdot}75$ g/cc $\quad \sigma = 1{\cdot}59$ g/cc
$\mu = 0{\cdot}0114$ poise $\quad X = 11{\cdot}1$ cm
$r_0 = 10{\cdot}8$ cm

Curve	*Figure*	S g solid / cc slurry	n' r.p.m.	$K \times 10^7$ g/sec.^{2}	$r_L = r_2$ cm	r_1 cm
A	2	0·10	1080	3·0	9·0	—
A, A′	4					
B	2	0·10	1080	3·0	9·0	10·0
C	2	0·10	1080	3·0	9·0	10·3
B	4					
D	2	0·10	1080	3·0	9·0	10·7
B′	4					
A	5	0·15	900	3·0	8·0	9·1
B	5	0·10	1200	3·2	7·73	9·62
C	5	0·15	1900	3·1	8·2	10·0
D	5	0·20	2100	3·0	7·7	10·5

Notation

C, C_1, C_2 = constant groups
g = gravitational acceleration — cm/sec.^{2}
K, K_0 = permeability — g/sec.^{2}
n = speed of revolution — r.p.s., n' r.p.m.
q = flow rate, q_L for liquid, q_s for slurry — cc/sec.
R_1, R_2 = constant groups
r = radius, r_c for cake inner surface, r_L for liquid surface, r_0 for cake outer surface, r_w for inner surface of basket wall — cm
s = slurry concentration ; (g air-dried material/cc slurry)
t = time — sec.
V = volume of slurry — cc
X = depth of basket — cm
x = height of cake — cm
μ = viscosity of liquid — poise
σ = density ; σ for air-dried solid ; σ_P for packing density — g/cc

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Extraction of acetic acid from water

3—Binary vapour-liquid equilibrium data

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(*Received* 4 *February* 1954)

Summary—This paper gives binary equilibrium data for the miscible systems benzene-acetic acid, ethyl acetate-acetic acid, acetic acid-water, and for the partially immiscible system ethyl acetate-water. Different values of the end activity coefficients are obtained for ethyl acetate and water, depending on the method of calculation. Furthermore, it is shown that in the immiscible region the extrapolated van Laar relationship does not hold.

Résumé—Données d'équilibre sur les systèmes binaires entièrement miscibles : benzène – acide acétique ; acétate d'éthyle – acide acétique ; acide acétique – eau ; et sur le système à miscibilité incomplète : acétate d'éthyle – eau. Suivant la méthode de calcul, on obtient pour le système acétate d'éthyle – eau des valeurs différentes pour les coefficients d'activité limites. En outre, dans la région d'hétérogénéité, la relation de Van Laar ne peut être extrapolée.

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Introduction

The purification of acetic acid by straight distillation is difficult due to the low relative volatility of acetic acid-water mixtures at high water concentrations. The separation of these two components has been simplified by employing solvent extraction followed by azeotropic distillation. The azeotropic distillation consists of feeding into the top of the column a third component which greatly increases the relative volatility of water to acetic acid and at the same time is only partially miscible with water.

Ethyl acetate has frequently been used commercially as the entrainer in this azeotropic separation but no vapour-liquid equilibrium data for the ethyl acetate-acetic acid-water system could be found in the literature. It is essential for the accurate design of an azeotropic column that the ternary vapour-liquid equilibrium data should be available or be capable of prediction from the binary data. In this instance, the prediction of the ternary equilibrium data from the binary data is complicated due to the association of acetic acid in the vapour state in both the binary and ternary systems. For this reason the binary and ternary vapour-liquid equilibria have been determined experimentally. The purpose of this paper is to present the vapour-liquid equilibria of the binary systems investigated.

Method of Analysis

The results on the benzene-acetic acid system were obtained using density determinations at 25°C and by titration with barium hydroxide solution for acetic acid as a check. The density values obtained are given in Table 8

Table 8
Densities of Benzene-Acetic Acid Mixtures

Mole % Benzene	*Density at 25°C*
0	1·0442
10·75	1·01193
13·2	1·00614
19·6	0·98873
37·6	0·95132
48·0	0·93338
71·2	0·90226
86·0	0·88522
100·0	0·8728

The ethyl acetate-acetic acid samples were analyzed using similar analysis methods. The densities obtained for mixtures of ethyl acetate and acetic acid at 25°C are given in Table 9.

Table 9

Densities of Acetic Acid-Ethyl Acetate Mixtures

Mole % *Ethyl Acetate*	*Density at 25°C*
0	1·0442
13·4	1·01356
28·9	0·98372
40·4	0·96527
61·9	0·93563
100·0	0·8945

The acetic acid-water samples were analyzed by determinations of the acetic acids by titration with barium hydroxide solution when less than 60% acetic acid by weight was present. If more than this amount was present the water content was determined by titration with Fischer reagent. The two methods were shown to agree over the range where both methods could be used.

The ethyl acetate-water samples were analyzed for water content using Fischer reagent.

Purity of Reagents

Acetic acid, ethyl acetate, benzene, water, were purified and analyzed as described in Part 1 [19] and Part 2 [23].

Equilibrium Determinations

The apparatus described by Ellis [24] was used in most cases, using essentially the same procedure. In certain cases where indicated a modified Gillespie [24] still was used. The temperature of the vapours leaving the still were maintained 1·2°C above that of the boiling liquid. Samples were drawn off into ice cooled bottles after 2-3 hours operation.

Vapour Pressure Data

The vapour pressures of benzene were calculated from the equation :

$$\log_{10} P\,(\text{mm Hg}) = 8{\cdot}11401 - 2046{\cdot}74\,\frac{1}{T(K)}$$

given by the National Bureau of Standards [25].

The vapour pressures of acetic acid were calculated from the equation

$$\log_{10} P\,(\text{mm Hg}) = 6{\cdot}89745 - \frac{1206{\cdot}35}{220\,(273 + t)}$$

given by Brown and Ewald [21].

The vapour pressure data for ethyl acetate were taken from International Critical Tables [26] and correlated by plotting $\log P$ vs. $\frac{1}{T}$.

Activity Coefficients

In this investigation activity coefficients have been calculated using the equation

$$\gamma_1 = \frac{\pi y_1}{P_1 x_1} \qquad (1)$$

where γ_1 = activity coefficient of component 1
π = total pressure
P_1 = vapour pressure of component 1 at the temperature of the determination
y_1 = mole fraction of component 1 in the vapour
x_1 = mole fraction of component 1 in the liquid

Benzene-Acetic Acid

The results given in Table 10a were calculated using the molecular weight of monomeric acetic acid. The results in Table 10b were calculated using the molecular weights of acetic acid vapour at the temperatures given. The molecular weight data by Ritten and Simons [27] were used. The results are expressed graphically on Fig. 6. It will be noticed that the results based on Table 10b are in much better agreement with the van Laar equations than the data of Table 10a.

Table 10*a*

Benzene-Acetic Acid

No.	*T°C*	X_B	Y_B	γ_B	X_A	Y_A	γ_A
1	111·2	3·0	15·2	2·12	97·0	84·8	1·08
2	92·3	22·0	56·2	1·8	78·0	43·8	1·31
3	89·3	29·3	62·8	1·64	70·7	37·2	1·37
4	86·5	38·0	69·0	1·50	63·0	31·0	1·43
5	84·7	45·8	72·5	1·39	54·2	27·5	1·55
6	83·3	55·0	77·5	1·29	45·0	22·5	1·60
7	82·1	65·3	81·5	1·19	34·7	18·5	1·80
8	81·1	75·0	85·3	1·11	25·0	14·7	2·04

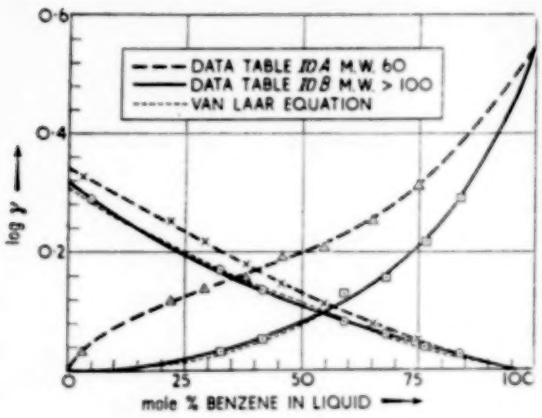

Fig. 6.

Table 10b
Benzene-Acetic Acid

No.	*T°C*	X_D	X_B	γ_B	X_A	Y_A	γ_A	*M.W. of Acetic Acid*
1	111·2	4·94	22·9	1·94	95·06	77·1	1·0	101·0
2	92·3	32·6	68·8	1·48	67·4	31·3	1·08	103·0
3	89·3	41·7	74·5	1·37	58·3	25·5	1·13	103·5
4	86·5	51·5	79·4	1·27	48·5	20·6	1·22	104·0
5	84·7	59·4	82·1	1·21	40·6	17·9	1·35	104·1
6	83·3	68·1	85·7	1·15	31·9	14·3	1·43	104·4
7	82·1	76·6	88·5	1·10	23·4	11·5	1·66	104·6
8	81·1	84·0	91·0	1·06	16·0	9·0	1·95	104·8

The evaluation of the activity coefficient of acetic acid in solution with another component is made difficult by association of acetic acid in the vapour state whether as a pure component or in a mixture. If acetic acid is present in a vapour mixture, and the second component does not alter the extent of association of the acetic acid compared with that of the acid in the pure state at that temperature, the associated acetic acid may be treated as a pure component (i.e. as distinct from a mixture of polymeric forms). The calculation of the liquid and vapour compositions is then made using the molecular weight of the acetic acid vapour at that temperature. If the second component in the mixture influences the state of association of the acetic acid in the vapour mixtures, the above procedure is no longer valid. The investigation of Raman spectra has shown that benzene does not influence the extent of association of acetic acid in liquid mixtures and it seems reasonable to assume that it will have no effect in the vapour state. It was thought, therefore, that if the molecular weight of the acetic acid in the pure vapour state at the relevant temperature be used to calculate the molar fractions in liquid and vapour mixtures of benzene and acetic acid, the activity coefficient curves will obey one of the equations given by Carlson and Colburn [13]. This procedure has been suggested previously by Butler [28] and by Herington [29].

In the comparison (Fig. 6) of experimental and van Laar activity coefficient plots, temperature and gas law deviation effects have been neglected.

Ethyl Acetate-Acetic Acid

The results obtained for this system are given in Tables 11a and 11b. together with the molecular weights used for acetic acid in calculating the mole fractions. The log activity coefficients given in Table 11b are plotted in Fig. 7. It can be seen that the deviation from ideality in this system is very small and consequently small errors in the

Table 11a
Ethyl Acetate-Acetic Acid

No.	*T°C*	X_A	X_E	Y_A	Y_E	γ_A	γ_E
1	79·5	12·8	87·2	2·24	97·8	·67	1·03
2	88·3	43·9	56·1	14·6	85·4	·92	1·09
3	93·6	58·0	42·0	26·8	73·2	1·05	1·05
4	99·7	98·5	28·6	41·1	58·9	1·06	1·04
5	105·1	81·8	18·2	57·8	42·2	1·07	1·01
6	108·1	86·3	13·8	67·3	32·7	1·07	·963

Table 11b
Ethyl Acetate-Acetic Acid

No.	*T°C*	X_A	X_E	Y_A	Y_E	γ_A	γ_E	*M.W. of Acetic Acid*
1	79·5	7·74	92·3	1·29	98·7	·64	·99	105
2	88·3	32·6	67·4	9·4	90·7	·79	·945	103·5
3	93·6	44·6	55·4	17·7	82·3	·90	·89	102·8
4	99·7	59·5	40·5	29·1	70·9	·905	·885	102
5	105·1	72·8	27·3	44·8	55·3	·931	·864	101·5
6	108·1	79·0	21·0	55·0	45·0	·96	·87	101·1

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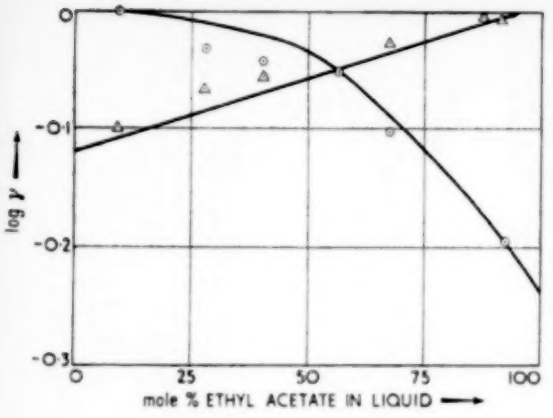

Fig. 7.

analysis of the vapour or liquid compositions markedly influence the log activity coefficients. Difficulty was experienced in analyzing mixtures by titration for acid when the acid was present in high concentrations. The results were checked by determining the density of the mixtures. Fig. 7 suggests that probably the best correlation of the experimental points is given by the two Margules curves. It seems possible that a certain amount of inter-association may take place giving curves which differ slightly from those in Fig. 7.

Acetic Acid-Water

The acetic acid-water system has been investigated quite extensively [21], [30], [31] with a variety of equilibrium stills. As there has been little consistency between the results obtained, it was decided to reinvestigate the system using the equilibrium still mentioned above.

Table 12*a*
Acetic-Acid Water

No.	*T°C*	X_A	X_W	Y_A	Y_W	γ_A	γ_W	$Y_W - X_W$
1	100·5	8·27	91·7	6·63	93·4	1·43	1·00	1·64
2	101·3	19·7	80·3	13·6	86·4	1·20	1·03	6·12
3	102·2	29·2	70·8	20·1	79·9	1·16	1·04	9·1
4	103·2	38·7	61·3	27·8	72·2	1·16	1·05	10·9
5	106·1	61·0	39·0	48·5	51·5	1·17	1·06	12·5
6	107·0	66·0	34·0	53·3	46·7	1·16	1·07	12·65
7	108·6	73·9	26·1	61·6	38·4	1·14	1·09	12·3
8	109·7	77·9	22·1	66·1	33·9	1·12	1·09	11·8
9	111·8	85·6	14·4	76·0	24·0	1·10	1·11	9·6
10	112·8	91·5	8·5	84·3	15·7	1·07	1·16	7·2
11	116·0	96·5	3·55	93·0	7·05	1·04		3·5
12	104·7	52·0	48·0	39·5	60·5	1·17	1·06	12·5

Table 12*b*
Acetic Acid Water

No.	*T°C*	X_A	X_W	Y_A	Y_W	γ_A	γ_W	*M.W.*
1	100·5	5·02	95·0	4·0	96·0	1·42	·995	102
2	101·3	12·6	87·4	8·5	91·5	1·17	1·00	101·8
3	102·2	19·6	80·4	12·9	87·1	1·11	1·00	101·8
4	103·2	27·1	72·9	18·5	81·5	1·10	1·00	101·7
5	106·1	51·5	48·5	38·1	61·9	1·09	1·03	101·3
6	107·0	53·5	46·5	40·4	59·6	1·08	1·00	101·2
7	108·6	62·6	37·4	48·9	51·1	1·06	1·01	101
8	109·7	67·6	32·4	53·6	46·4	1·05	1·02	101
9	111·8	78·0	22·0	65·4	34·6	1·04	1·04	100·9
10	113·8	86·5	13·5	76·4	23·6	1·03	1·09	100·7

The results obtained are listed in Tables 12a and 12b. For the purpose of comparison of the data with that obtained by previous investigations a plot of y_1-x_1 for water was made. These values are given in Table 12a and plotted in Fig. 8. The results obtained in this investigation

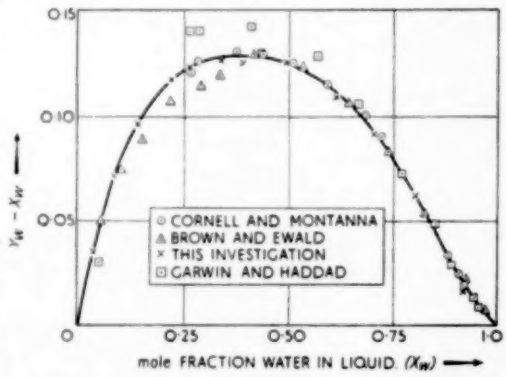

Fig. 8.

agree well with those of Cornell and Montonna [30] and are in reasonable agreement with those of Brown and Ewald [21]. The results of Garwin and Haddad have a slightly higher relative volatility in the middle portion of the concentration range but agree well with the present data at the extremities.

The log activity coefficients for this system are plotted in Fig. 9. Correction for the molecular

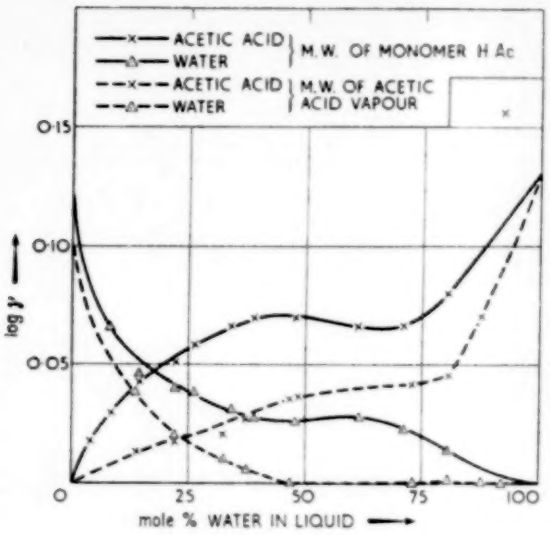

Fig. 9.

weight of acetic acid in the vapour still does not give a reasonable correlation. This is probably due to the change in the degree of association of acetic acid when diluted with water as pointed out by TRAYNARD [31]. No correlation of this system was attempted in the absence of quantitative data on the change in association of acetic acid vapour in the presence of water vapour.

ETHYL ACETATE-WATER SYSTEM

The activity coefficients of the two components in the ethyl acetate-water binary system are considerably higher than those for the ethyl acetate-acid and water acetic acid systems. In the prediction of ternary equilibrium data in the ternary ethyl acetate-acetic acid-water system from those of the binary systems the activity coefficients of the ethyl acetate-water system are therefore the controlling ones. Unfortunately, this binary system is the most difficult to investigate experimentally.

As may be seen from Fig. 10, the ethyl acetate-water system presents the particular difficulty of being immiscible in both the liquid and vapour condensate phases over the greater part of the concentration range. Any liquid concentration falling within the range *AB* will give a vapour of composition represented by *D*. This means

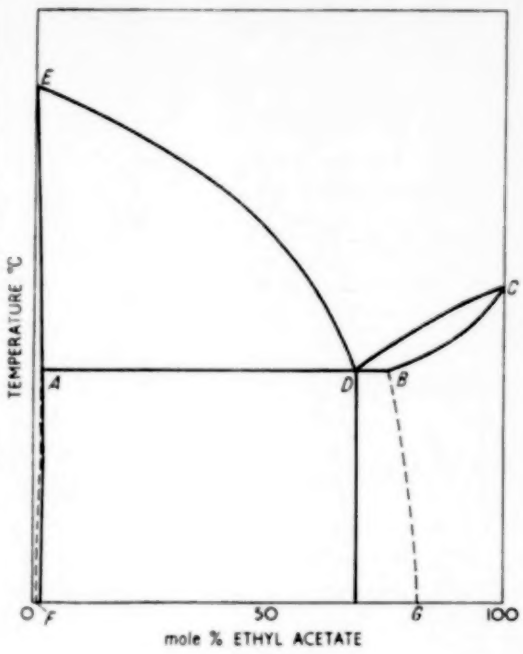

Fig. 10.

that, once this azeotrope composition has been determined, only the vapour-liquid equilibria of liquids with compositions between *A* and *E* and *B* and *C* have to be investigated. The analysis at each end of the composition range is thus liable to be inaccurate. The composition at *A* for the ethyl acetate-water system is only between 1 and

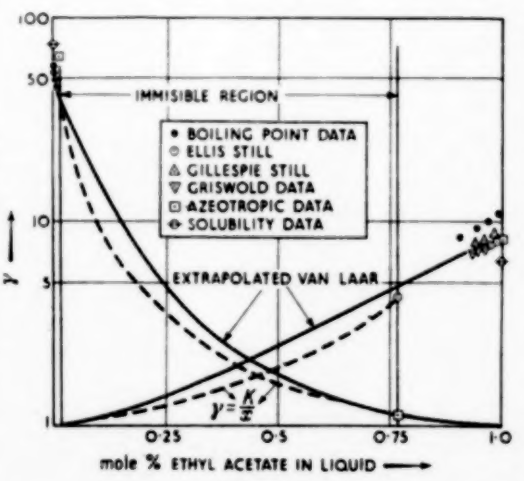

Fig. 11.

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2 mole %. A further problem concerning the equilibrium determinations is that over a considerable portion of the above concentration ranges, the vapour condensate will be two-phase due to the composition being within the miscibility boundary *FA BG*.

Table 13 lists the vapour liquid equilibrium results obtained for this system and these terminal results are plotted on Fig. 11. The composition of the azeotrope was found to be 69·7 mole per cent ethyl acetate which agrees well with other results in the literature.

Table 13
Ethyl Acetate-Water System

$T°C$	X_E	Y_E	X_W	Y_W	γ_E	γ_W	*Still*
74·8	97·1	91·4	2·86	8·64	1·02	8·04	G
75·6	98·3	94·7	1·69	5·28	1·02	8·04	G
75·7	98·6	95·4	1·41	4·59	1·02	8·34	G
75·0	97·4	92·7	2·59	7·33	1·02	7·47	E
75·9	98·4	95·3	1·57	4·67	1·05	7·6	E

In all, three methods were used for the prediction of end values (i.e., $\log \gamma_A$ at $X_A = 0$, $\log \gamma_B$ at $X_B = 0$ etc.) of the activity coefficients of this system. These were as follows :

(a) by experimental determination of the vapour-liquid equilibria when the liquid and vapour condensate are both single phases ;

(b) from the azeotrope composition and the composition of the two liquid phases in equilibrium. When the boiling liquid mixture is partially immiscible, the activities of these phases will be equal and consequently each liquid phase will be in equilibrium with the azeotropic vapour composition ;

(c) by using the boiling points of the miscible liquid mixtures between 0-1 mole % and 90-100 mole % of ethyl acetate and extrapolating these activity coefficients to find the end values.

GRISWOLD *et al.* [32] have investigated the vapour-liquid equilibria of the ethyl acetate-water system and obtained an end value of 8·0 for the activity coefficient curve of water. In the eventual correlation, however, GRISWOLD used the solubility equations given by COLBURN and SCHEONBORN [33] and end values of 6·5 and 76 were obtained for water and ethyl acetate respectively.

CARLSON and COLBURN have stated that the solubility equations are known to give results which vary considerably from those obtained from vapour liquid equilibrium determinations. This arises from the assumption that in the original derivation of the solubility equation the van Laar or Margules equations are valid.

The activity coefficient end values for water obtained in the present investigation are given as follows :

(a)	Vapour liquid equilibria data	8·3
(b)	From azeotrope determinations	8·3
(c)	From boiling point measurements	11·0

The results obtained from boiling point data have been found to be higher than those obtained from equilibrium determinations. This would be expected since the method of calculation is based on an approximation. Thus the figure of 8·3 would appear to be best of the end values for the activity coefficient of water in this mixture.

The end values obtained for ethyl acetate are as follows :

(a)	From vapour liquid equilibria	48·0
(b)	From azeotropic data	65·4
(c)	From boiling point data	50·0

The vapour liquid equilibrium results for ethyl acetate in water were determined on a still used by SELVEPATNAM [34] in which both the immiscible liquid and vapour condensate mixtures were stirred.

The above activity coefficient end values have been mainly determined from the activity coefficients of miscible mixtures which exist up to the extremities of the two-phase boundaries and of these values the first is preferred.

In considering the immiscible region two problems arise :

(a) Can the binary van Laar curves in the miscible region be extrapolated into the miscible region and expressed in terms of the overall composition of the liquid phases ?

(b) Can the binary van Laar curves be extrapolated in the increased miscible region produced by the presence of the third component ?

HERINGTON [29] has stated that within the two phase regions it is possible to use activity coefficients based on the overall composition of the liquid. Assuming this is correct then the activity coefficients in the immiscible region are defined as follows :

$$\log \gamma_1 = \log \frac{\pi y_1}{P_1 x_1} = \log \frac{K_1}{x_1} \qquad (2)$$

$$\log \gamma_2 = \log \frac{\pi y_2}{P_2 x_2} = \log \frac{K_2}{x_2} \qquad (3)$$

K_1 and K_2 are constants since in the immiscible region the temperature is constant and a heterogeneous azeotrope is formed giving constant values of y_1 and y_2 for binary composition x_1 and x_2. Thus if the temperature and azeotrope composition is known, K_1 and K_2 can be evaluated.

Equations (2) and (3) are of a different form from either the van Laar or Margules equations and consequently when plotted on Fig. 11 for ethyl acetate-water the curves for equations (2) and (3) do not coincide with the extrapolated van Laar curves ; therefore it would appear that the binary van Laar curves in the miscible region cannot be extrapolated into the immiscible region.

From Fig. 11, it is interesting to note that the activity coefficients for the boundary compositions evaluated from equations (2) and (3) are lower than those evaluated from the extrapolated van Laar curves in the miscible region. Whilst this difference may be within experimental error, ROBINSON and GILLILAND [35] also refer to the deviation from the van Laar equations of experimental data of systems approaching immiscibility and suggest that this is due to entropy effects occurring on mixing. Thus, until further experimental work is available, question (b) cannot be satisfactorily answered ; this information is, however, essential for the accurate prediction of vapour liquid equilibria in the immiscible ternary region.

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NOTATION

P = vapour pressure
T = temperature °K
t = temperature °C
π = total pressure
y_1 = mole fraction of component 1 in the vapour
x_1 = mole fraction of component 1 in the liquid
γ = activity coefficient
K_1, K_2 = constants

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Liquid-liquid extraction in a "rotating disc contactor"

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(*Received* 19 *February* 1954)

Summary—Using the system water-acetic acid-methyl isobutyl ketone, the extraction performance of a "rotating disc contactor" (R.D.C.) of small diameter was investigated for various values of the rotor speed, total throughput and solvent to feed ratio. By comparing the separating efficiency with the fractional volume of the dispersed phase under the same circumstances, it was found that under certain conditions the efficiency decreases, although the hold-up of the dispersed phase increases. This effect is ascribed to back-mixing in the continuous phase due to entrainment by the dispersed phase.

The effectiveness of the R.D.C. is compared with that of similar extraction columns.

Résumé—En employant le système de l'eau-acide acétique-méthylisobuty'cétone l'extraction à contre-courant dans un "rotating disc contactor" (R.D.C.) a été examinée pour plusieurs valeurs de la vitesse rotatoire, du débit total des liquides, et du rapport entre les débits des deux liquides. Une comparaison entre l'efficacité de séparation et le volume fractionnel de la phase dispersé sous les mêmes conditions montre qu'en certains cas l'efficacité diminue pendant que la teneur en phase dispersée augmente. Ceci est attribué au mélange longitudinale dans la phase continue dû à l'entrainement par la phase dispersée.

L'efficacité de l'R.D.C. est comparée à celle des colonnes d'extraction semblables.

Introduction

During the past few years several new types of extraction apparatus have been described which show a greater efficiency and a better operational flexibility than the more conventional types (sieve-tray column, packed column, spray tower). In particular we refer to extraction columns which have a rotating element : the Scheibel extractor [1], [2], the "rotating core column" [3], [4], the "multi-stage mixer column" [5] and the "rotating disc contactor" [6]. In these extraction columns, the intimacy of the contact between the two liquid phases depends primarily on the rotor speed. By adjustment of this new independent variable the most favourable conditions for a given extraction process can be achieved.

To determine these conditions the influence of the main operating variables, i.e. rotor speed, total throughput and solvent to feed ratio, on the extraction performance of a rotating disc contactor (R.D.C.) was investigated. At the same time the relative hold-up of the dispersed phase was determined under various conditions. A comparison of the column efficiency and the hold-up was made since both of these quantities are related to the interfacial area between the two phases.

In this work no attempt was made to investigate the effect of the dimensions or the constructional details of an R.D.C. on the separating efficiency. Neither were the conditions investigated under which flooding occurs. The extraction experiments were restricted to one system only, the well-known system water-acetic acid-methyl isobutyl ketone (MIBK).

Experimental Details

(a) *The liquid system*

There were several reasons for choosing the system water-acetic acid-MIBK :

1. The acid content can easily be determined by titration with NaOH to the phenol phthaleïn endpoint.
2. The distribution ratio of acetic acid between water and MIBK is near unity, and depends but little on the concentration of the acid or the temperature.
3. The system shows little tendency to form stable emulsions except after prolonged use.

4. Since this system has been used by many other investigators a comparison of the performance of different types of equipment is possible.

Equilibrium measurements had previously been carried out in this laboratory. The results were in close agreement with those of SCHEIBEL and KARR [2], which have been used for further calculations (see Table 1). For the densities of both phases, which depend on solute concentration, the data published by OLDSHUE and RUSHTON [5] were used.

Table 1.
Equilibrium distribution of acetic acid between water and MIBK at 20°C.

Acid content of MIBK-phase (x, kg/m^3)	0	10·0	20·0	30·0	40·0
Acid content of water-phase (y, kg/m^3)	0	20·0	38·5	55·8	71·4

In all experiments to be described acetic acid was extracted from MIBK with acid-free water. Before each run the water- and MIBK-phases were saturated with respect to each other. After the extraction, the resulting extract phase containing water, some acid and a small amount of MIBK was discarded. The raffinate phase (MIBK) was recirculated for further use.

The acid content of the MIBK feed varied between 3 and 5 per cent by weight. At these low concentrations both the equilibrium line and the operating line are sufficiently straight to justify the use of a rapid numerical calculation of the efficiency. Furthermore, the physical characteristics do not change appreciably during the extraction process. Only the interfacial tension cannot be sufficiently controlled; even at low acid contents it depends markedly on the concentration. Moreover, its value is affected by the inevitable small amounts of impurities.

(b) *The extraction column*

Fig. 1 shows the construction and the dimensions of the " rotating disc contactor " used. It consists of a vertical cylindrical tube fitted with a number of horizontal flat rings, spaced at equal distances. The rotor, which is mounted coaxially, is provided with a number of equally spaced flat discs.

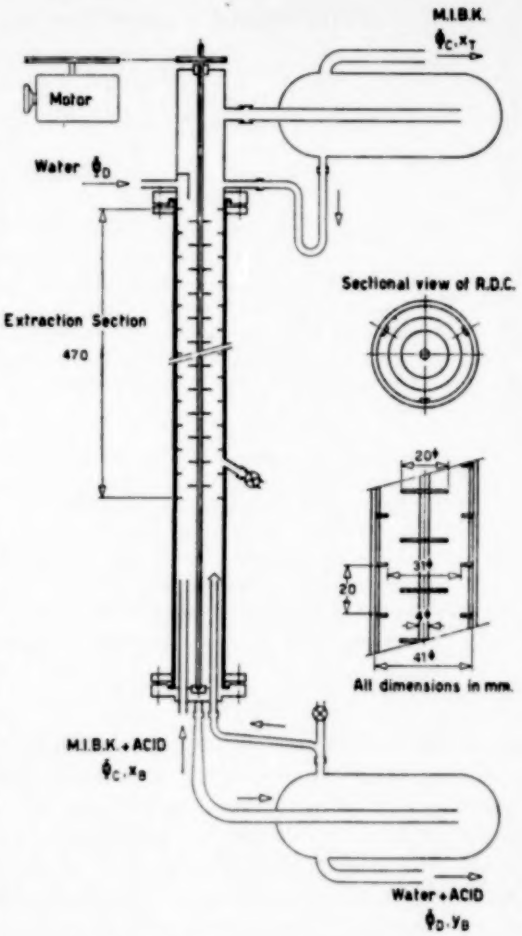

Fig. 1. The extraction column (R.D.C.).

As has been pointed out by REMAN [6] in his original paper on the R.D.C., the turning of the rotor generates in the liquid in each compartment two toroïdal vortices, which rotate in the horizontal plane. In this way a rather uniform degree of turbulence is produced, the intensity of which is governed by the rotor speed for given dimensions and liquid system. It is believed that by this arrangement an emulsion of relatively uniform drop size is produced since spots with excessive turbulence or very high rates of shear are absent.

The top and bottom parts of the column contain the bearings of the rotor and the feed and exit lines for both liquid phases. Top and bottom were provided with an after-settler as indicated

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in Fig. 1, with return lines for the heavy and light phase respectively. In most runs these settlers appeared to be superfluous, since nearly all of the settling took place in the free space in the top and bottom of the column. Separate experiments proved that the amounts of acid extracted in the settlers were negligible.

In view of the corrosive nature of the system used, the column was constructed of stainless steel. The bearings were of a self-lubricating material, *Philite*. Neoprene rubber was used as a packing material. Because of some swelling, this had to be renewed several times during the year.

(c) *Auxiliary equipment*

This was of conventional nature. The feed and solvent were fed from high reservoirs by gravity and the incoming flow rates were controlled by means of stainless steel needle valves and measured with calibrated rotameters. All runs mentioned here were performed with the heavy (water) phase dispersed in the light (MIBK) phase. By adjusting the bottom discharge stream (either manually or automatically with an on-off controller responding to changes in dielectric constant) the interface between the two liquid phases in the lower settler was kept at a constant level.

For reasons mentioned above, all parts were made of glass or stainless steel. For junctions between glass and steel lines natural rubber tubing, which had to be replaced from time to time, was used.

PROCEDURE AND CALCULATIONS

(a) *Extraction*

Before starting a run the entire column was filled with MIBK, which contained the acetic acid to be extracted (concentration x_b), and the MIBK flow rate was fixed at a desired value. After that the acid-free water was fed into the top of the column at a constant desired flow rate. A steady operation was obtained after 15 to 30 minutes. Attainment of the steady state was checked by rapid calculation of the material balance of the acetic acid from the observed flow rates, x_b, and the acid contents of the MIBK- and water-phase leaving the extractor (x_t and y_b respectively). In general this material balance checked within 2 to 3%. All experiments were carried out at room temperature, i.e. between 17 and 22°C.

The efficiency of the extraction operation was calculated in terms of the product of K_D, the overall mass transfer coefficient with reference to the dispersed (water) phase, and the total area of interfacial contact A. Since the equilibrium and the operating lines were approximately straight, K_DA could be calculated from the simple equation :

$$\Phi_D y_b = K_D A\,(\Delta y)_{l.m.}, \qquad (1)$$

where

$$(\Delta y)_{l.m.} = \frac{(y_b^* - y_b) - y_t^*}{\ln\,[(y_b^* - y_b)/y_t^*]}. \qquad (2)$$

The values of y_b^* and y_t^* (in equilibrium with x_b and x_t respectively) were taken from a graph of the equilibrium relationship between x and y.

The use of equation (1) is justified provided there is no back-mixing in either phase. The values of K_DA are mean values for the whole column under the conditions prevailing at the time of the measurement.

The column efficiency has also been evaluated in terms of the "height equivalent to one theoretical stage" (H.E.T.S.) according to the method of VARTERESSIAN and FENSKE [7]. For these calculations the effective height of the column was taken to be 0·47 m.

(b) *Holdup*

For the determination of the fractional volume of dispersed phase (ϕ_D) several methods can be used. For instance, at a certain moment all feed and exit lines can be closed simultaneously, after which the fractional volume of water in the column can be measured. This method does not give the true average ϕ_D of the extraction section since the liquid in the top and bottom parts is included in such measurements.

In principle ϕ_D can be found by determining the average density of the liquid in the extraction section by a manometric method. Results obtained in this way were not sufficiently accurate because of the short length of the column and because of wetting difficulties ; moreover, there were small

additional pressure effects due to the swirling motion of the liquid in the column.

The method finally adopted consisted of suddenly draining a part of the contents of the extraction section and determining the fractional water content after this sample had settled. To this end the column had been fitted with a short side-tube near the lower end of the extraction section (see Fig. 1). By suddenly opening a wide-bored stopcock in this tube during normal operation of the extractor, an amount of 150 to 250 ml. (about 1/3 of the total volume) was drained from the extraction section within a few seconds. Smaller samples reduced the precision of the ϕ_D observed; if samples larger than 250 ml. were taken, a part of the continuous phase below the extraction section was entraind.e

These relative hold-up measurements were always carried out in duplicate. In 75% of the cases the two determinations checked within 5%.

Discussion of Results

Two series of experimental runs were performed: one in which the solvent to feed ratio was kept constant ($\Phi_D/\Phi_C = 1$), and the total throughput was varied ($12 < (\Phi_D + \Phi_C) < 60$ l/hr), and a second in which Φ_D/Φ_C was varied between 0·25 and 4 at a constant total throughput ($\Phi_D + \Phi_C$) of 30 l/hr. In both series four different rotor speeds were used (350, 600, 1200 and 1800 r.p.m.). The efficiencies and ϕ_D-values are reported in Tables 2 and 3.

(a) *Efficiency*

Fig. 2 shows that K_DA is approximately proportional to the total throughput if the solvent to feed ratio is kept constant. The value of K_DA at a constant throughput, however, passes through a maximum when the value of Φ_D/Φ_C is varied (Fig. 3). This maximum is located at a value of Φ_D/Φ_C between 1 and 2 when $\Phi_D + \Phi_C = 30$ l/hr.

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Table 2.

Extraction efficiency and fractional volume of dispersed phase in R.D.C. (I.D. = 4·1 cm) $\Phi_D/\Phi_C = 1$.

No. of run	*Rotor speed r.p.m.*	*Water Φ_D l/hr.*	*MIBK x_b kg/m³*	*MIBK x_t kg/m³*	*Water y_b kg/m³*	$10^2 \times \phi_D$	$10^6 \times K_DA$ m_3/sec.	*H.E.T.S. m*
1	350	7·0	31·0	14·7	17·0	3·6	1·0	0·80
2	350	10·0	32·5	12·7	21·2	4·9	1·8	0·55
3	350	15·0	32·5	13·6	20·5	7·1	2·6	0·61
4	350	22·5	31·0	11·8	19·0	10·3	3·9	0·58
5	350	30·0	36·1	14·2	22·1	14·6	5·2	0·59
6	600	7·0	22·4	8·85	14·0	3·0	1·2	0·54
7	600	10·0	36·2	11·5	25·6	4·5	2·3	0·43
8	600	15·0	36·0	11·9	25·3	6·2	3·3	0·45
9	600	20·0	22·4	8·21	14·1	8·9	4·2	0·54
10	600	20·0	39·1	12·8	26·2	9·2	4·3	0·46
11	600	25·0	32·6	10·6	21·8	11·5	5·2	0·46
12	600	30·0	32·6	11·1	21·4	15·2	6·0	0·48
13	1200	7·0	25·9	7·24	19·5	2·7	1·8	0·39
14	1200	10·0	34·1	9·10	27·3	4·4	2·8	0·36
15	1200	15·0	35·2	8·05	27·9	8·6	4·7	0·33
16	1200	20·0	34·0	6·67	27·1	13·3	6·4	0·30
17	1200	25·0	25·9	4·25	21·0	33·6	8·9	0·27
18	1800	6·0	26·8	4·81	22·5	3·7	2·2	0·26
19	1800	10·0	26·8	4·02	23·8	7·4	4·2	0·23
20	1800	15·0	29·6	2·97	27·0	16·2	7·8	0·18
21	1800	15·0	23·2	2·81	20·9	13·7	6·9	0·21
22	1800	15·0	39·1	3·65	35·1	16·7	8·2	0·19

Table 3. Extraction efficiency and fractional volume of dispersed phase in R.D.C. (I.D. = 4·1 cm). $\Phi_D + \Phi_C = 30$ l/hr.

No. of run	*Rotor speed r.p.m.*	Φ_D/Φ_C	*MIBK* x_b *kg/m³*	*MIBK* x_t *kg/m³*	*Water* y_b *kg/m³*	$10^2 \times \phi_D$	$10^6 \times K_D A$ *m³/sec*	*H.E.T.S.* *m*
23	350	0·25	38·1	30·4	30·3	3·1	1·1	0·88
(3)	350	1·0	32·5	13·6	20·5	7·1	2·6	0·61
24	350	2·0	38·6	7·48	15·7	8·6	2·9	0·46
25	350	4·0	38·6	3·54	8·80	9·7	2·3	0·45
26	600	0·25	37·4	29·0	36·0	3·4	1·4	0·70
27	600	0·50	26·3	14·9	22·8	4·8	2·3	0·60
(8)	600	1·0	36·0	11·9	25·3	6·2	3·3	0·45
28	600	2·0	26·3	5·67	11·1	7·8	2·8	0·48
29	600	3·0	29·0	4·20	8·82	9·1	2·4	0·46
30	600	4·0	29·0	2·80	7·06	9·4	2·4	0·45
31	1200	0·25	27·8	18·4	36·4	4·4	2·5	0·45
32	1200	0·50	27·9	12·4	30·9	5·5	3·7	0·36
(15)	1200	1·0	35·2	8·05	27·9	8·6	4·7	0·33
33	1200	2·0	35·2	3·06	16·8	10·4	4·7	0·31
34	1200	2·0	45·2	3·71	21·0	9·5	4·8	0·32
35	1200	4·0	32·0	1·04	7·85	11·9	3·4	0·33
36	1800	0·25	22·0	12·5	36·5	6·7	4·7	0·23
37	1800	0·25	32·0	17·8	53·3	7·6	5·4	0·20
38	1800	0·28	29·3	12·5	45·6	9·2	6·5	0·20
39	1800	0·5	29·6	8·86	41·1	11·1	7·1	0·19
40	1800	0·5	23·2	7·32	31·3	9·3	6·3	0·22
(20)	1800	1·0	29·6	2·97	27·0	16·2	7·8	0·18
(21)	1800	1·0	23·2	2·81	20·9	13·7	6·9	0·21
(22)	1800	1·0	39·1	3·65	35·1	16·7	8·2	0·19
41	1800	2·0	29·3	1·00	14·7	19·2	6·4	0·21

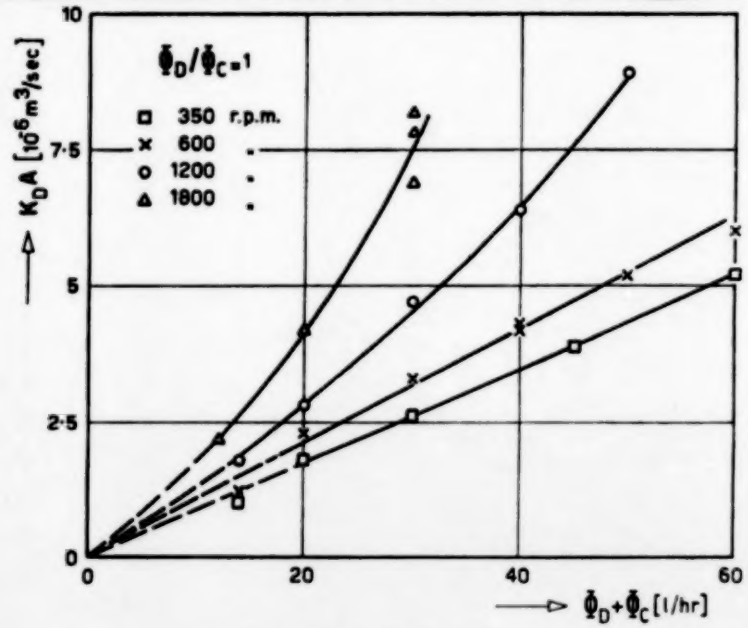

Fig. 2. $K_D A$ vs total throughput.

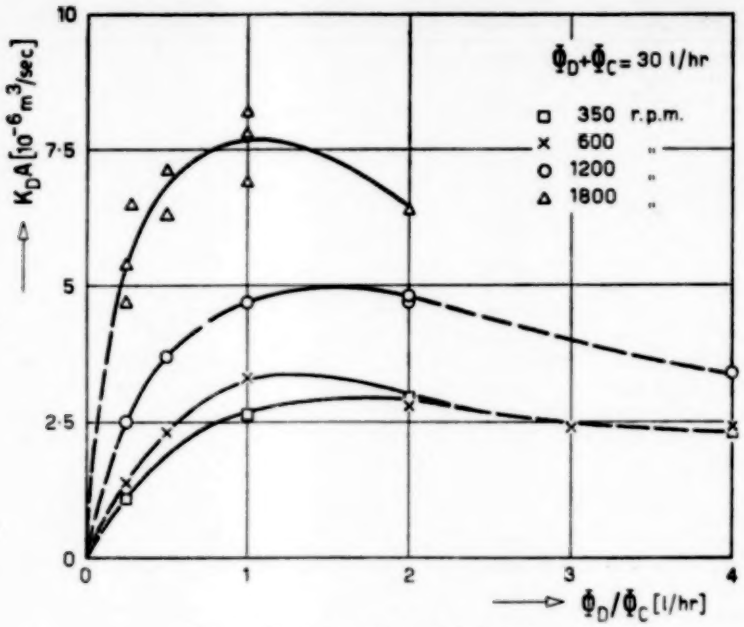

Fig. 3. K_DA vs. solvent to feed ratio.

An increase of the rotor speed markedly improves the efficiency of the column because the average drop size of the dispersed phase becomes smaller. As a result of this, of course, the maximum throughput of the column is limited to a lower value. In these experiments, for

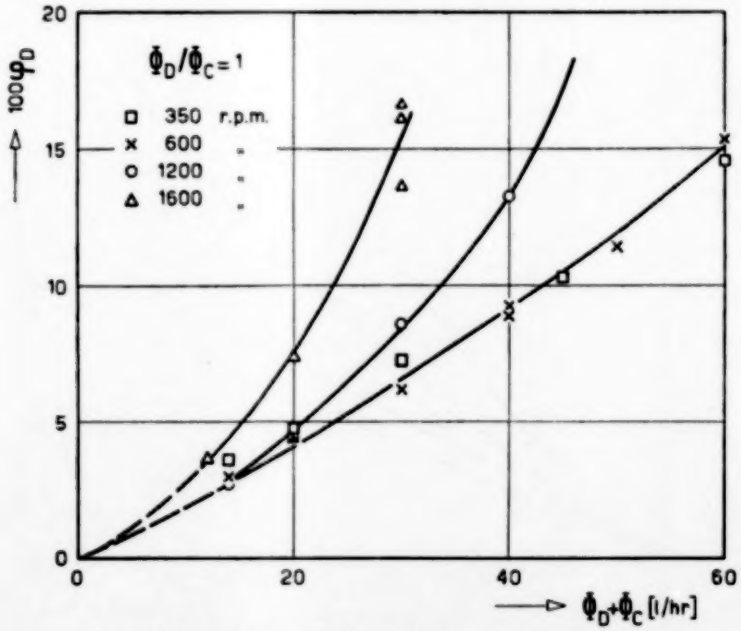

Fig. 4. Volume fraction of dispersed phase vs. total throughput.

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instance, the maximum total flow rate ($\Phi_D+\Phi_C$) for $\Phi_D/\Phi_C = 1$ was about 35 l/hr at 1800 r.p.m. and 50 l/hr at 1200 r.p.m.

As can be seen from Tables 2 and 3, the H.E.T.S. values of the column are influenced primarily by the rotor speed. Under favourable conditions, i.e. not too small a liquid load and Φ_D/Φ_C of the order of unity, the H.E.T.S. appear to be about 20, 30, 45 and 60 cm for 1800, 1200, 600 and 350 r.p.m. respectively.

(b) *Volume fraction of dispersed phase*

The hold-up measurements reported in Tables 1 and 2 were preceded by a preliminary investigation concerning the influence of flow rates and rotor speed on ϕ_D. Throughout these preliminary runs the binary system water-MIBK was used in order to avoid variations in physical properties, in particular surface tension. Consequently these results showed much less scattering than the values reported for actual extraction conditions. The latter ϕ_D values were always somewhat higher than those obtained with the binary system under the same conditions.

Figs 4 and 5 show that ϕ_D increases with increasing rotor speed and with increasing flow rate of the dispersed phase, as was to be expected.

(c) *Relation between K_DA and ϕ_D*

Figs. 2 and 4 and also the left-hand side of Figs. 3 and 5 show great similarity which suggests a parallel between K_DA and the fractional volume of the dispersed phase. Therefore in Fig. 6 these two quantities have been plotted for various values of the rotor speed. A rather good proportionality between K_DA and ϕ_D is observed as long as ϕ_D does not exceed the value of 0·15 and Φ_D/Φ_C is not much greater than 1.

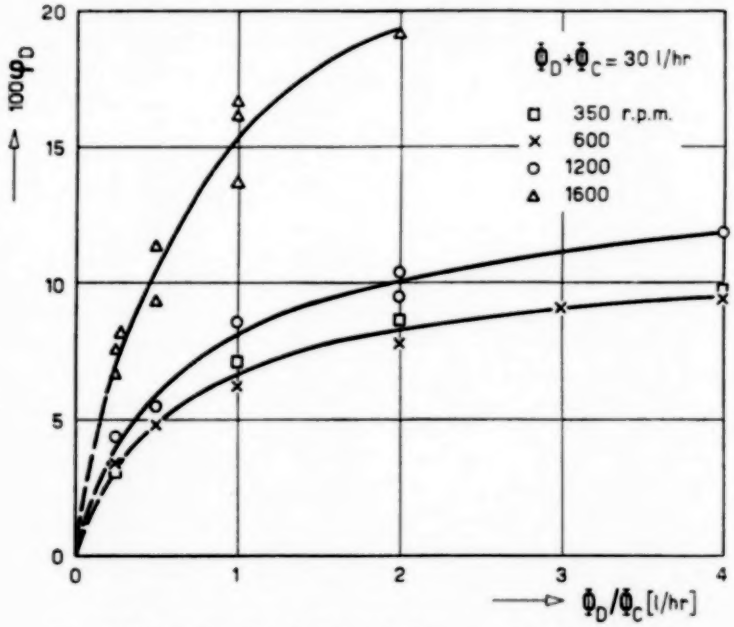

Fig. 5. Volume fraction of dispersed phase vs. solvent to feed ratio.

As has been noted by APPEL and ELGIN [8], SHERWOOD, EVANS and LONGCOR [9], JOHNSON and BLISS [10] and GIER and HOUGEN [11], under certain conditions in spray towers there is a proportionality between K_DA and ϕ_D. In these cases it is assumed that both these quantities are directly proportional to the number of drops of the dispersed phase per unit volume, with the mean drop size remaining constant. For spray

towers the latter will be approximately true, since for a given system the drop size is primarily determined by the nozzle construction.

In the R.D.C. the drop size distribution depends mainly on the flow conditions in the extractor, which are determined primarily by

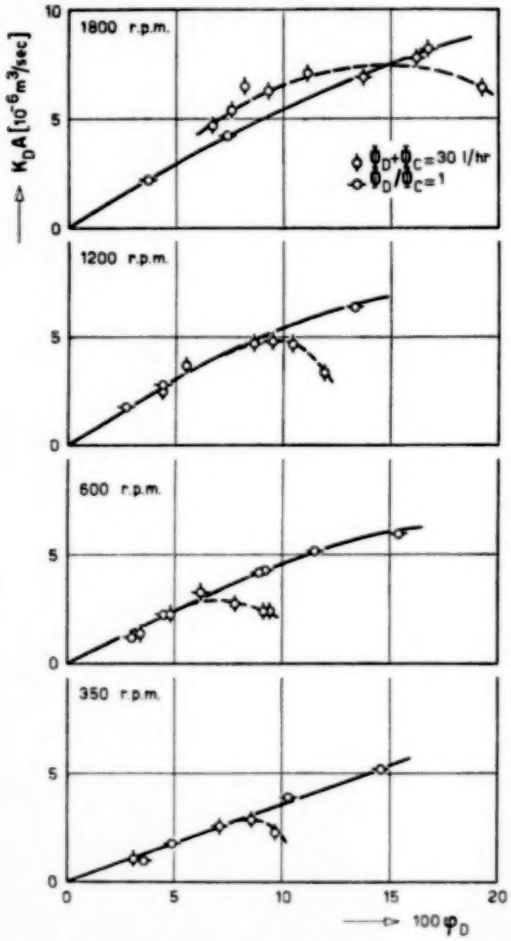

Fig. 6. Relationship between $K_D A$ and fractional hold-up of dispersed phase. (— — — —) = constant throughput and varying solvent to feed ratio ; (————) = constant solvent to feed ratio and varying throughput.

the rotor speed, so a proportionality between $K_D A$ and ϕ_D can be expected for a constant speed of the rotor.

Fig. 6 shows that this relationship between $K_D A$ and ϕ_D obtains if the hold-up is increased by increasing the total throughput at a constant value of Φ_D/Φ_C of unity.

If, on the other hand, ϕ_D is increased by increasing the solvent to feed ratio, Φ_D/Φ_C, while the total throughput is kept constant, the value of $K_D A$ passes through a maximum. The most probable explanation for this is that at high Φ_D/Φ_C values the continuous phase is entrained by the dispersed phase to a marked extent. This special kind of " back-mixing " in the continuous phase impairs the efficiency of the extraction operation. This is reflected in the relatively low values of $K_D A$, as calculated by means of equations (1) and (2), since these equations are not valid when appreciable back-mixing occurs in one or both phases. Similar effects have been observed by GIER and HOUGEN [11] and been mentioned by OLDSHUE and RUSHTON [5].

In our experiments, at a value of $\Phi_D/\Phi_C > 1$ the back-mixing effect appears to become important irrespective of the rotor speed and the hold-up. This conclusion should not be generalised however, since not only the solvent to feed ratio, but also the equilibrium relationship and the column efficiency itself determine for a certain type of column the conditions at which back mixing is significant. As the effect is of importance for the operation of most extraction columns with a high efficiency and a relatively small volume, further study is desirable, especially of the entrainment and subsequent mixing of the continuous phase.

COMPARISON WITH OTHER EQUIPMENT

REMAN [6] has pointed out that for a comparison of different types of extraction equipment both the efficiency (e.g. expressed in H.E.T.S.) and the flow of liquid handled should be taken into account. As an index of effectiveness of operation he proposed : I_e = total throughput/volume of one theoretical stage. In Table 4 a number of values of this index have been collected for the system water-acetic acid-MIBK. As far as possible, the most favourable examples were taken from the literature. Strictly speaking the comparison is not complete, if the value of Φ_D/Φ_C, the choice of the dispersed phase, the

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Table 4.

Comparison of effectiveness of different types of extraction equipment.

Type of column	*Reference*	*Dispersed phase*	*Solvent*	Φ_D/Φ_C	*Acid content in feed weight %*	*Rotor speed, r.p.m.*	*Column I.D., m*	*H.E.T.S m*	*Effectiveness index I_e min^{-1}*
Core	[3] Table I No. 25	water	water	0·83	6	1000	0·021	0·094	0·8
Core	[3] Table I No. 44	water	water	1·35	6	1000	0·021	0·15	0·7
Core	[3] Table I No. 53	water	water	0·57	6	1075	0·012	0·029	1·9
Scheibel	[2] Table VII No. 75	MIBK	MIBK	1·0	15-20	400	0·287	0·24	1·4
Scheibel	[2] Table VII No. 85	MIBK	water	1·0	15-20	693	0·287	0·32	1·5
Scheibel	[2] Table VII No. 96	water	MIBK	1·0	15-20	560	0·287	0·24	1·7
Scheibel	[2] Table VII No. 93	water	water	1·0	15-20	400	0·287	0·32	1·5
Scheibel	[2] Table VII No. 100	water	MIBK	1·0	15-20	400	0·287	0·23	2·1
Scheibel	[1] Table 12 No. 18	?	MIBK	abt. 1	20	1680	0·025	0·086	1·4
Scheibel	[1] Table 12 No. 19	?	MIBK	abt. 1	20	1680	0·025	0·056	2·2
Scheibel	[1] Table 12 No. 20	?	MIBK	abt. 1	20	1680	0·025	0·061	2·0
Mixer	[5] Table 16 No. 12	MIBK	MIBK	2·0	3	300-	0·153	0·14	2·5
Mixer	[5] Table 16 No. 4	MIBK	MIBK	2·0	3	-450	0·153	0·099	2·0
R.D.C.	[6] Fig. 8	water	water	1·0	?	1835	0·079	0·061	3·3
R.D.C.	[6] Fig. 8	water	water	2·0	?	1835	0·079	0·059	3·4
R.D.C.	Authors } not reported	MIBK	water	2·0	3-5	1200	0·041	0·21	1·9
R.D.C.	Authors } in this paper	MIBK	water	1·0	3-5	1800	0·041	0·21	3·2
R.D.C.	Authors }	MIBK	water	1·0	3-5	1200	0·041	0·25	1·6
R.D.C.	Authors Nos. 20-22	water	water	1·0	3-5	1800	0·041	0·19	2·1
R.D.C.	Authors No. 41	water	water	2·0	3-5	1800	0·041	0·21	1·9

acid concentration and the direction of mass transfer are different. Roughly it can be said, however, that there is not much difference between the "multi-stage mixer column" [5] and the R.D.C., which in fact are very similar to each other. On the average the SCHEIBEL columns show somewhat lower figures; they have relatively small H.E.T.S. values, but their specific capacity is also lower than that of the two other types of extractors mentioned.

ACKNOWLEDGMENT

We owe much to Ir. K. R. WESTERTERP, who constructed the apparatus, determined the equilibrium concentrations and performed a great number of preliminary measurements, and to J. M. DE MUINCK KEIZER who participated in a part of this investigation. We also thank Dr. G. H. REMAN (*Royal Dutch/Shell Laboratory, Amsterdam*) for his interest in this work and his valuable discussions.

NOTATION

A = total interfacial area in extractor
I_e = "effectiveness index," total throughput divided by volume per theoretical extraction stage
K_D = overall mass transfer coefficient with reference to the dispersed phase
x = acid concentration in MIBK-phase
y = acid concentration in water-phase
ϕ_D = volume fraction occupied by dispersed phase
Φ_C = continuous phase volume flow rate (here MIBK)
Φ_D = dispersed phase volume flow rate (here water)

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Chemical Engineering Science, 1954, Vol. 3, pp. 65 to 73. Pergamon Press Ltd.

The sedimentation of a suspension of uniform spheres under conditions of viscous flow

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(*Received* 18 *February* 1954)

Summary—The dynamic equilibrium of a suspension of uniform spherical particles settling in a fluid has been considered, and an expression has been obtained for the drag force on a constituent particle. This has been expressed in the form of a correction factor to be used in conjunction with Stokes' Law, and has been compared with the correction factor obtained from experimental measurement. Two configurations of particles have been considered and good agreement has been obtained between the theoretical and experimental correction factors at volumetric concentrations greater than about 0·05, though the correction factor extrapolates to zero, corresponding to zero drag on the particle, at infinite dilution. The reasons for this di crepancy are discussed.

Résumé—Etude de l'équilibre dynamique de la sédimentation dans un fluide d'une suspension de particules sphériques uniformes : établisement d'une expression pour la friction. Cette dernière est donnée sous forme d'un terme correctif s'ajoutant à la loi de Stokes ; elle a été comparée au terme correctif déduit des résultats experimentaux. Les auteurs ont etudié deux configurations des particules et ont obtenu un accord satisfaisant entre les facteurs de correction theorique et experimental tant que la concentration volumétrique dépasse 0,05, bien que ce facteur puisse s'extrapoler jusqu' à zero, correspondant ainsi á une friction nulle, pour une dilution infinie. Discussion des raisons de ce désaccord.

In 1851 Stokes [1] obtained a theoretical expression for the drag force (F) acting on a single spherical particle moving relative to a continuous fluid.

$$F = 3\pi\mu V d \qquad (1)$$

where μ = viscosity of the fluid,
d = diameter of the sphere,
V = relative velocity.

The fluid was assumed infinite in extent and the relative velocity low so that the inertia of the fluid could be neglected. Equation (1) has been tested experimentally and found accurate at low velocities; for a Reynolds Group with respect to the particle of less than 0·2, the error does not exceed 4%.

Since many industrial operations, such as sedimentation, elutriation, and fluidization, involve relative motion between a fluid and a system of suspended particles, it is important to be able to predict the forces acting on the particles, and hence their settling rate in the fluid. A number of experimental studies have been made and empirical relations developed for the effect of concentration on the rate of sedimentation of suspensions of particles, but no satisfactory theoretical treatment of the problem has emerged.

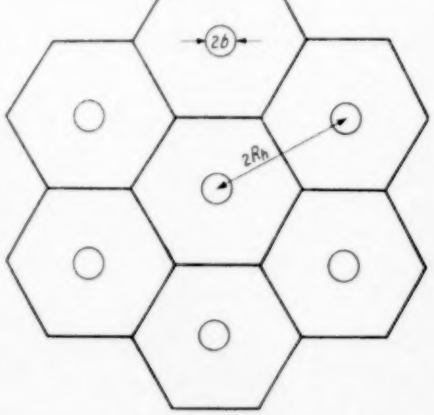

Fig. 1a. Hexagonal pattern.

In the present paper a number of simplifying assumptions have been made to enable a theoretical treatment to be applied to the problem of the sedimentation of a uniformly dispersed suspension of spheres under conditions where the resistance is due entirely to viscous drag. Because the suspension settles at a constant rate and forms a sharp interface, it is assumed that all the particles are settling at the same constant velocity and that a statistically stable arrangement is maintained.

In order to simplify calculations, McNown [2] suggested that each particle in a suspension could be regarded as being situated in the centre of a hexagon of fluid as indicated in Fig. 1a. The vertical distances between the layers were taken as equal to the distance between the particles in a horizontal direction (Arrangement 1, Fig. 1b).

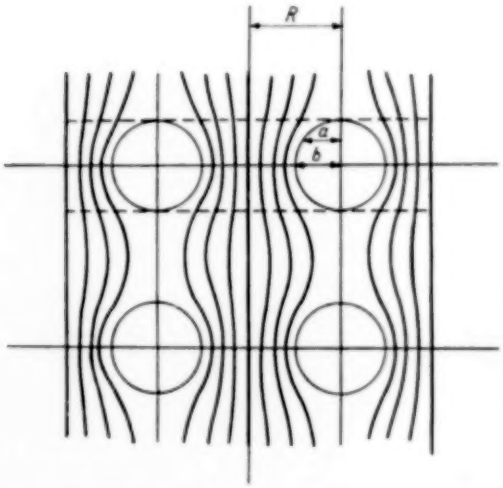

Fig. 1b. Particle configuration (*I*) $b/R = 1{\cdot}126\sqrt[3]{C}$ at 10% volumetric concentration.

On the other hand, Hawksley [2] considered the particles to be arranged in adjacent horizontal layers so as to offer the minimum resistance to the motion of a fluid flowing through the system (Arrangement 2, Fig. 1c). In this second arrangement, it is assumed that the hexagonal pattern in a horizontal plane is retained. The relation between the volumetric concentration of particles (C) and the ratio of the particle radius ($b = d/2$)

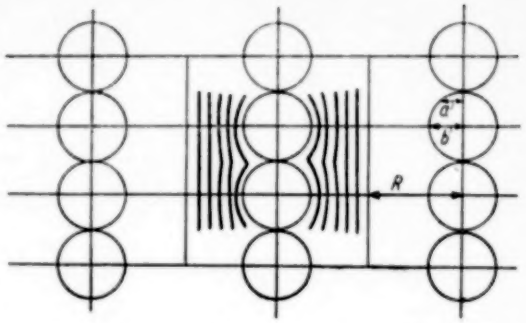

Fig. 1c. Particle configuration (*II*) $b/R = 1{\cdot}225\sqrt{C}$ at 10% volumetric concentration.

to the distance between the centres of the particles in a horizontal plane ($2R_h$) is then obtained as follows :

Arrangement 1

Volume of each hexagonal prism $= 4\sqrt{3}\,R_h^3$

$$\text{Volumetric concentration} = C = \frac{\frac{4}{3}\pi b^3}{4\sqrt{3}\,R_h^3} = \frac{\pi}{24\sqrt{3}}\left(\frac{b}{R_h}\right)^3$$

$$\therefore \frac{b}{R_h} = 1{\cdot}183\sqrt[3]{C} \qquad (2)$$

Arrangement 2

Volume of hexagonal prism $= 4\sqrt{3}\,R_h^2\,b$

$$\text{Volumetric concentration} = C = \frac{4\pi b^3}{3}\cdot\frac{1}{2\sqrt{3}\,R_h^2 d}$$

$$\therefore \frac{b}{R_h} = 1{\cdot}286\sqrt{C} \qquad (3)$$

In order to simplify the boundary conditions, it is assumed that each particle is surrounded by a cylinder of fluid with the same cross-sectional area as the hexagonal prism, so that the radius, R, of the cylinder is given by

$$\pi R^2 = 2\sqrt{3}\,R_h^2$$

and

$$\frac{R}{R_h} = 1{\cdot}05$$

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For the first configuration

$$\frac{b}{R} = \frac{1{\cdot}183}{1{\cdot}05}\sqrt[3]{C} = 1{\cdot}126\sqrt[3]{C} \qquad (4)$$

and for the second :

$$\frac{b}{R} = \frac{1{\cdot}286}{1{\cdot}05}\sqrt{C} = 1{\cdot}225\sqrt{C} \qquad (5)$$

The resistance force to the motion of a " representative " particle is dependent on the distances between the particles in the horizonatal layers. In the first configuration the particles are closer and therefore the velocity gradients are steeper and the drag is greater for a given mean relative velocity.

Equations of Flow

For convenience we shall regard the particles as stationary and the free surface of the fluid as moving upwards at a velocity V_c ; this problem is equivalent to that of a suspension settling at a velocity V_c relative to a fixed horizontal plane.

Let r be the radius of an elementary ring of the fluid round a particle, dl be the thickness of the ring in the direction of the streamlines, and dn the width along the equipressure lines as shown in Fig. 2.

V is the velocity of the fluid along a streamline at point (r, h) and θ is the angle between the streamline and the vertical.

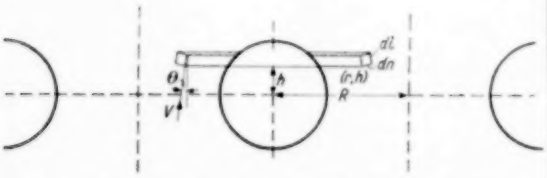

Fig. 2. Diagram of elementary ring of fluid round a particle.

Equilibrium of the Ring

Since the ring of fluid is in equilibrium, the resultant shearing force balances the force due to the difference in fluid pressure, P.

Thus

$$\frac{\partial}{\partial n}\left(2\pi r\, dl \,.\, \frac{\partial V}{\partial n} \,.\, \mu\right) dn = \frac{\partial}{\partial l}\left(2\pi r\, dn \,.\, P\right) dl$$

$$\therefore 2\pi\mu \,.\, \frac{\partial}{\partial n}\left\{(dl)\left(r\frac{\partial V}{\partial n}\right)\right\} dn = 2\pi \,.\, \frac{\partial}{\partial l}\left\{(dn)\,(rP)\right\} dl$$

$$\therefore \mu\left\{dl \,.\, \frac{\partial}{\partial n}\left(r\frac{\partial V}{\partial n}\right) dn + r\frac{\partial V}{\partial n} \,.\, \frac{\partial}{\partial n}(dl)\, dn\right\}$$

$$= \left\{dn\,\frac{\partial}{\partial l}(rP)\, dl + r\,P\,\frac{\partial}{\partial l}(dn)\, dl\right\}$$

Since

$$\frac{\partial}{\partial n}(dl)\, dn = \frac{\partial \theta}{\partial l}\, dl \,.\, dn \qquad (6a)$$

and

$$\frac{\partial}{\partial l}(dn)\, dl = \frac{\partial \theta}{\partial n}\, dn \,.\, dl \qquad (6b)$$

(see Fig. 3).

$$\therefore \mu\left\{dl \,.\, \frac{\partial}{\partial n}\left(r\frac{\partial V}{\partial n}\right) dn + r\frac{\partial V}{\partial n} \,.\, \frac{\partial \theta}{\partial l}\, dl \,.\, dn\right\}$$

$$= \left\{dn \,.\, \frac{\partial}{\partial l}(r\,P)\, dl + r\,P\,\frac{\partial \theta}{\partial n}\, dn \,.\, dl\right\}$$

i.e.

$$\mu\left\{\frac{\partial}{\partial n}\left(r\frac{\partial V}{\partial n}\right) + r\frac{\partial V}{\partial n}\frac{\partial \theta}{\partial l}\right\} = \left\{\frac{\partial}{\partial l}(rP) + rP\frac{\partial \theta}{\partial n}\right\} \qquad (7)$$

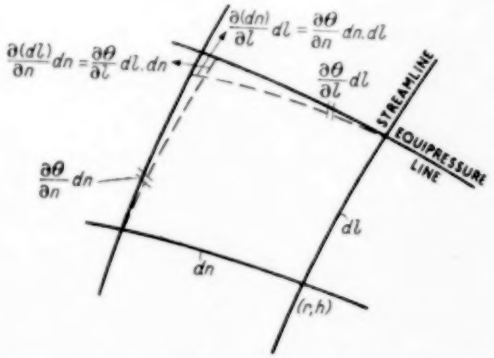

Fig. 3. Enlarged diagram of the element a, b, c, d.

Continuity

The rate of flow of fluid through the elementary ring $= V \,.\, 2\pi r\, dn$.

Since the rate of flow between two streamlines is constant,

$$\frac{\partial}{\partial l}(V \cdot 2\pi r\, dn) = 0$$

i.e.

$$\frac{\partial (rV)}{\partial l} \cdot dn + rV \frac{\partial}{\partial l}(dn) = 0$$

From equation (6b),

$$\frac{d(rV)}{\partial l} \cdot dn + rV \frac{\partial \theta}{\partial n} dn = 0$$

i.e.

$$\frac{\partial (rV)}{\partial l} + rV \frac{\partial \theta}{\partial n} = 0 \qquad (8)$$

Boundary Conditions

The flow must be symmetrical with respect to adjacent particles and the velocity at the surface of each particle is zero

$$\therefore \frac{\partial V}{\partial n} = 0 \qquad \text{at} \qquad r = R$$

and

$$V = 0 \qquad \text{at} \qquad r = a = \sqrt{b^2 - b^2}$$

Resultant Shearing Force on Sphere

Consider a ring of length dl at the surface of the sphere, as shown in Fig. 4. The shearing force on the ring can be resolved into a vertical and a horizontal component; the net horizontal component must be zero.

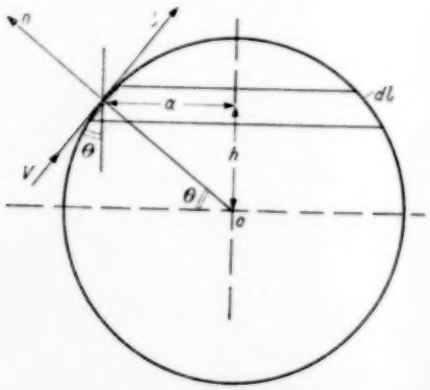

Fig. 4. Diagram of elementary ring on the surface of a particle.

The vertical force on the ring

$$= 2\pi a\, dl\, \mu \left(\frac{\partial V}{\partial n}\right)_{r=a} \cos\theta = 2\pi a\, \mu \left(\frac{\partial V}{\partial n}\right)_{r=a} dh$$

(since $dl \cos\theta = dh$).

$\therefore$ resultant force on sphere

$$= \int_{-b}^{b} 2\pi a\, \mu \left(\frac{\partial V}{\partial n}\right)_{r=a} dh \qquad (9)$$

In order to simplify the above equations and to enable a solution to be obtained, it will be assumed that $\partial P/\partial h$ is constant at a given horizontal plane at all points between $r = a$ and $r = R$. This is equivalent to taking the value of the angle θ between the streamlines and the vertical as very small; this will not be appreciably in error, except near the surface. We therefore take

$$\cos\theta = 1$$

Equation (7) then becomes

$$\mu \frac{\partial}{\partial n}\left(r \frac{\partial V}{\partial n}\right) = \frac{\partial (rP)}{\partial l}$$

$$= P \frac{\partial r}{\partial l} + r \frac{\partial P}{\partial l}$$

$$= r \frac{\partial P}{\partial l} \quad \left(\because \frac{\partial r}{\partial l} = \sin\theta\right)$$

$$\therefore \int \frac{\partial}{\partial n}\left(r \frac{\partial V}{\partial n}\right) dn = \frac{1}{\mu} \int r \frac{\partial P}{\partial l} dn \qquad (10)$$

Now since $P = f(r, h)$

$$\frac{\partial P}{\partial l} = \frac{\partial P}{\partial h} \cdot \frac{\partial h}{\partial l} + \frac{\partial P}{\partial r} \cdot \frac{\partial r}{\partial l}$$

$$\approx \frac{\partial P}{\partial h}$$

(taking $\frac{\partial h}{\partial l} = \cos\theta \approx 1$ and $\frac{\partial r}{\partial l} = \sin\theta$ which is small).

Thus from equation (10),

$$r \frac{\partial V}{\partial n} = \frac{1}{\mu} \int r \frac{\partial P}{\partial h} dr \quad \left(\text{since } \frac{\partial r}{\partial n} = \cos\theta \approx 1\right)$$

$$= \frac{1}{\mu} \frac{\partial P}{\partial h} \cdot \frac{r^2}{2} + k$$

(where k is an integration constant).

$$\therefore \frac{\partial V}{\partial n} = \frac{1}{\mu}\frac{\partial P}{\partial h}\frac{r}{2} + \frac{k}{r}$$

When $r = R$, $\frac{\partial V}{\partial n} = 0$

$$\therefore k = -\frac{1}{\mu}\frac{\partial P}{\partial h}\frac{R^2}{2}$$

and

$$\frac{\partial V}{\partial n} = \frac{1}{2\mu}\frac{\partial P}{\partial h}\left(r - \frac{R^2}{r}\right) \qquad (11)$$

Since

$$\frac{\partial r}{\partial n} = \cos\theta \approx 1$$

$$\frac{\partial V}{\partial r} = \frac{1}{2\mu}\cdot\frac{\partial P}{\partial h}\left(r - \frac{R^2}{r}\right) \qquad (12)$$

On integration,

$$V = \frac{1}{2\mu}\cdot\frac{\partial P}{\partial h}\left(\frac{r^2}{2} - R^2\ln r\right) + k'$$

At $r = a$, $V = 0$

$$\therefore k' = -\frac{1}{2\mu}\frac{\partial P}{\partial h}\left(\frac{a^2}{2} - R^2\ln a\right)$$

$$\therefore V = \frac{1}{2\mu}\frac{\partial P}{\partial h}\left(\frac{r^2-a^2}{2} - R^2\ln\frac{r}{a}\right) \qquad (13)$$

The mean velocity V_c of flow of fluid based on the total area of the cylinder of radius R is given by

$$\pi R^2 V_c = \int_{r=a}^{r=R} V\cos\theta \cdot 2\pi r\, dr$$

Substituting for V from equation (13) and putting $\cos\theta = 1$,

$$\pi R^2 V_c = \int_{r=a}^{r=R}\frac{1}{2\mu}\frac{\partial P}{\partial h}\left(\frac{r^2-a^2}{2} - R^2\ln\frac{r}{a}\right)2\pi r\, dr$$

$$= \frac{\pi}{\mu}\frac{\partial P}{\partial h}\left[\frac{r^4}{8} - \frac{r^2a^2}{4} - a^2R^2\left(\frac{r^2}{2a^2}\right)\left(\ln\frac{r}{a} - \frac{1}{2}\right)\right]_{r=a}^{r=R}$$

$$\therefore \frac{\partial P}{\partial h} = \frac{\mu V_c}{\frac{3}{8}R^2\left\{1 + \frac{1}{3}\left(\frac{a}{R}\right)^4 - \frac{4}{3}\left(\frac{a}{R}\right)^2 - \frac{4}{3}\ln\frac{R}{a}\right\}} \qquad (14)$$

The force on the sphere

$$F = \int_{-b}^{+b} 2\pi a\mu\left(\frac{\partial V}{\partial n}\right)_{r=a} dh \text{ (equation 9).}$$

From equation (11), we have

$$\left(\frac{\partial V}{\partial n}\right)_{r=a} = \frac{1}{2\mu}\frac{\partial P}{\partial h}\left(a - \frac{R^2}{a}\right)$$

$$\therefore F = \int_{-b}^{+b} 2\pi a\mu\left\{\frac{1}{2\mu}\cdot\frac{\partial P}{\partial h}\left(a - \frac{R^2}{a}\right)\right\} dh$$

$$= \pi\int_{-b}^{+b} R^2\left\{\frac{\partial P}{\partial h}\left[\left(\frac{a}{R}\right)^2 - 1\right]\right\} dh$$

$$= \frac{8}{3}\pi V_c\mu\int_{-b}^{+b}\left(\frac{\left(\frac{a}{R}\right)^2 - 1}{1 + \frac{1}{3}\left(\frac{a}{R}\right)^4 - \frac{4}{3}\left(\frac{a}{R}\right)^2 - \frac{4}{3}\ln\frac{R}{a}}\right) dh$$

$$= 2\left(\frac{8}{3}\pi V_c\mu b\right)\int_0^1\left(\frac{\left(\frac{a}{R}\right)^2 - 1}{1 + \frac{1}{3}\left(\frac{a}{R}\right)^4 - \frac{4}{3}\left(\frac{a}{R}\right)^2 - \frac{4}{3}\ln\frac{R}{a}}\right)\frac{dh}{b}$$

$$= 3\pi\mu V_c d\left(\frac{8}{9}\int_0^1\left(\frac{\left(\frac{a}{R}\right)^2 - 1}{1 + \frac{1}{3}\left(\frac{a}{R}\right)^4 - \frac{4}{3}\left(\frac{a}{R}\right)^2 - \frac{4}{3}\ln\frac{R}{a}}\right)\frac{dh}{b}\right) \qquad (15)$$

$$= 3\pi\mu V_c d(\beta_t) \qquad (16)$$

where β_t is a theoretical correction factor for use in conjunction with Stokes' Law; its value is dependent only on the concentration.

Table 1. γ as a function of a/R

a/R	γ
0	0
0·001	0·1218
0·005	0·1651
0·01	0·1947
0·03	0·2717
0·05	0·3328
0·1	0·4752
0·2	0·7987
0·3	1·2599
0·4	1·9656
0·5	3·1819
0·6	5·4566
0·7	10·6136
0·8	25·597
0·9	143·57
0·95	832·7
1	

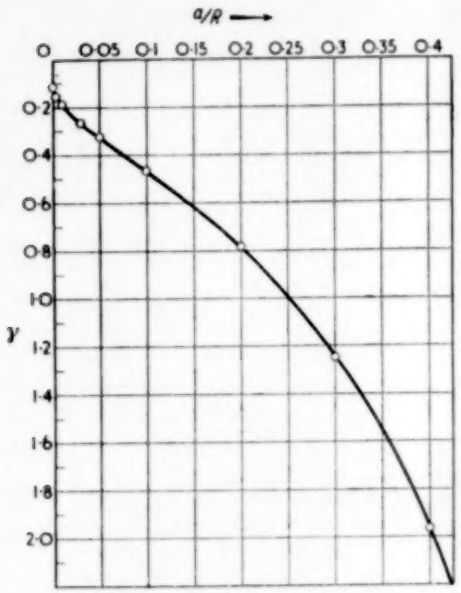

Fig. 5(*a*).

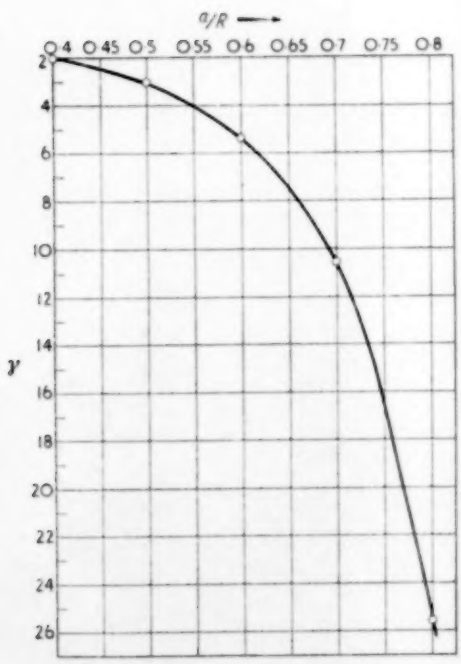

Fig. 5(*b*)

Fig. 5. γ as a function of a/R (3 graphs.)

In order to facilitate the graphical evaluation of the integral in equation (15), values of γ are calculated for various values of a/R (Table 1) and plotted (Fig. 5).

Here

$$\gamma = \left(\frac{\left(\frac{a}{R}\right)^2 - 1}{1 + \frac{1}{3}\left(\frac{a}{R}\right)^4 - \frac{4}{3}\left(\frac{a}{R}\right)^2 - \frac{4}{3}\ln\frac{R}{a}} \right)$$

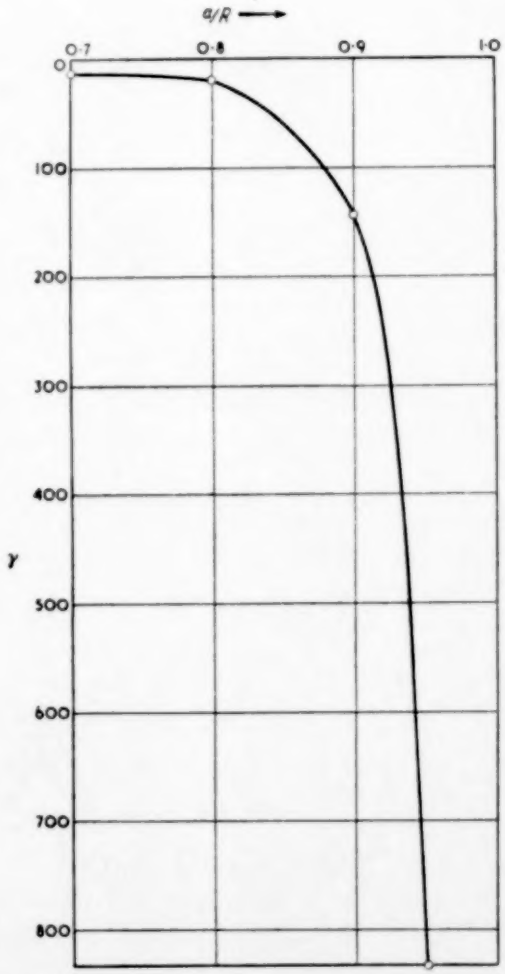

Fig. 5(*c*)

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Table 2

C	$\beta_e = e^{-4.65C}$	$b/R = 1.225\sqrt{C}$ configuration II		$b/R = 1.126\sqrt[3]{C}$ configuration I	
		b/R (II)	β_t	b/R (I)	β_t
0·05	1·271	0·274	0·78	0·415	1·32
0·1	1·634	0·388	1·188	0·523	2·11
0·15	2·128	0·474	1·68	0·599	2·99
0·2	2·818	0·548	2·335	0·659	4·15
0·25	3·806	0·612	3·21	0·71	5·62
0·3	5·248	0·671	4·407	0·754	7·58
0·35	7·413	0·725	6·36	0·794	10·5
0·4	10·73	0·775	8·815	0·83	15·1
0·45	15·98	0·821	13·8	0·864	23·4
0·5	25·12	0 866	24 37	0·894	38·5
0·55	40·83	0·909	51·27	0·921	69
0·606	75·86	0·9525	190	0·9525	190

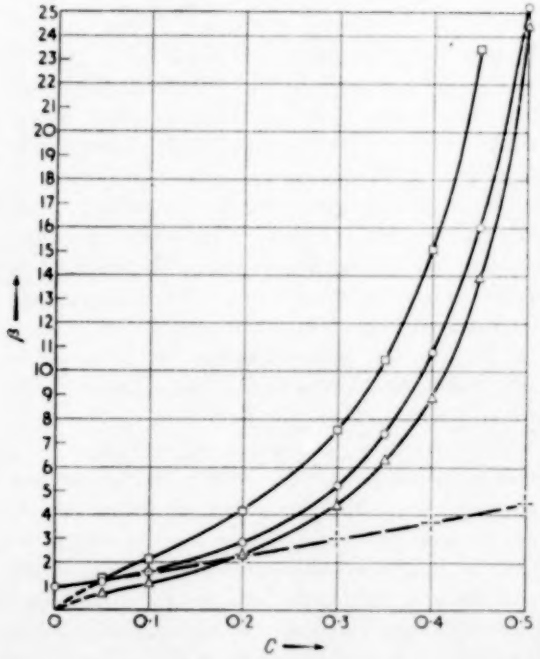

Fig. 6. Experimental or theoretical correction factors vs. concentration

- o Expermental correction factor vs. concentration.
- Δ Theoretical correction factor (configuration II) vs. concentration.
- □ Theoretical correction factor (configuration I) vs. concentration.
- + Theoretical correction factor (BURGERS) vs. concentration.

In Table 2, values of b/R and β_t are given for the two configurations as a function of the volumetric concentration C, and β_t is plotted against C in Fig. 6.

A sample calculation is given below in Table 3.

Table 3. *Sample calculation.* Evaluation of the theoretical correction factor for $b/R = 0.548$

h/b	$1-(h/b)^2$	$\frac{a}{b}=\sqrt{1-\left(\frac{h}{b}\right)^2}$	$\frac{a}{R}=\frac{b}{R}\cdot\frac{a}{b}$	γ
0	1	1	0·548	4·12
0·1	0·99	0·99499	0·545	4·09
0·2	0·96	0·9798	0·536	3·87
0·4	0·84	0,91652	0·502	3·23
0·6	0·64	0·8	0·439	2·37
0·8	0·36	0·6	0·329	1·43
0·9	0·19	0·4358	0·239	0·96
0·99	0·0199	0·14107	0·0774	0·41
1	0	0	0	0

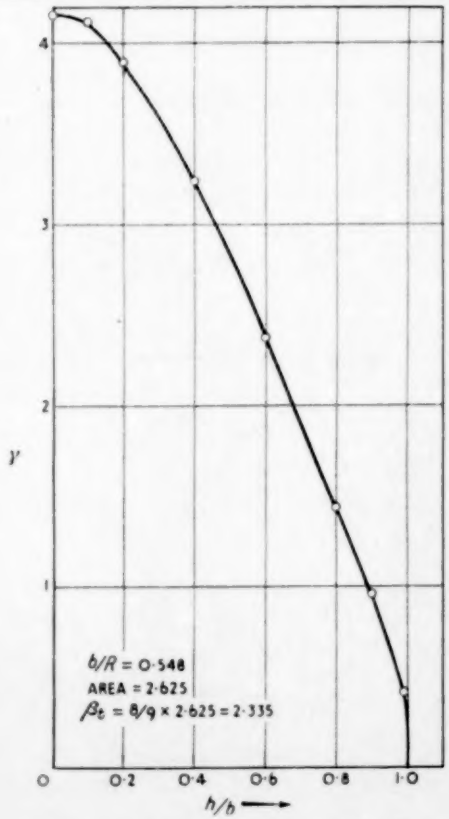

Fig. 7. Graphical evaluation of $\int_0^1 \gamma \frac{dh}{b}$.

γ is plotted against h/b in Fig. 7, and the area under the curve is 2·625. Hence the theoretical correction factor $= 8/9 \times 2{\cdot}625 = 2{\cdot}335$.

Experimental Verification

The results of a study of the sedimentation and fluidisation of particles of various shapes, including spheres, has been reported elsewhere [4]. For conditions of viscous flow, a relation was obtained, connecting the terminal falling velocity of a single spherical particle in an infinite medium (V_0) with the velocity of fall (V_c) of suspension of uniform spherical particles contained in a vessel where diameter was large compared with that of the particle.

$$V_c = V_0\, \epsilon^{4{\cdot}65} \tag{17}$$

where ϵ = the voidage of the suspension ($=1-C$)

$$\therefore\ V_c = V_0\,(1 - C)^{4{\cdot}65} \tag{18}$$

For a single particle settling at its terminal falling velocity, we have

$$F = 3\pi\,\mu\, V_0\, d = \frac{\pi d^3}{6}\,(\rho_s - \rho)\, g$$

i.e.
$$V_0 = \frac{d^2\,(\rho_s - \rho)\, g}{18\mu} \tag{19}$$

and for a particle in a suspension

$$F = 3\pi\,\mu\, V_c\, d\, \beta_e = \frac{\pi d^3}{6}\,(\rho_s - \rho)\, g$$

i.e.
$$V_c = \frac{d^2\,(\rho_s - \rho)\, g}{18\,\mu\,\beta_e} = \frac{V_0}{\beta_e} \tag{20}$$

where β_e is an experimentally determined correction factor from Stokes' Law. Comparing equations (18) and (20).

$$\beta_e = (1 - C)^{-4{\cdot}65} \tag{21}$$

Values of β_e, are plotted against the volumetric concentration C, in Fig. 6, and are seen to lie between the two theoretical values. It would therefore appear that the configuration of particles is intermediate between the two theoretical arrangements and that arrangement 1 is approached more closely, especially at high concentrations.

Also shown in Fig. 6, as a broken line, are the results of a theoretical analysis by Burgers [6], who investigated the effect of concentration on the settling velocity of a suspension of spheres. He concluded that for a random distribution of particles

$$V_c = V_0\,(1 + 6{\cdot}875\, C)^{-1} \tag{22}$$

The agreement between Burgers' theoretical expression and the experimental data is poor except at concentrations less than 0·2. The results of the present theory agree quite closely at high concentrations but extrapolate to give a correction factor of zero instead of unity at infinite dilution. This error appears to have a parallel in "Stokes' Paradox," discussed by Birkhoff [5], in which the drag force exerted on a section of an infinitely long cylinder, with its axis parallel to the direction of flow, extrapolates to zero as the radius of the boundary walls approach infinity.

The error in the present theoretical work appears to arise because an average pressure gradient $\partial P/\partial h$, has been used in the calculation of the drag force on particles of the suspension. At relatively high concentrations $\partial P/\partial h$ is finite but at very low concentrations $\partial P/\partial h$ tends to zero and it is not therefore permissible to substitute for it.

The theoretical treatment is, of course, not rigorous because no exact solution of the problem is possible with the mathematical techniques at present available, and it has been necessary to make assumptions about the distribution of the particles and the angles between the streamlines and the direction of flow. At high concentrations however a reasonably satisfactory correlation of the theoretical and practical figures has been obtained.

Acknowledgment

The authors are indebted to Professor D. M. Newitt, F.R.S., in whose laboratories the experimental work was carried out, for his constant help and encouragement.

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Notation

a	= radius of circle at height (h) from centre of sphere = $\sqrt{b^2 - h^2}$	L
b	= radius of sphere	L
C	= volumetric concentration	—
d	= diameter of sphere	L
F	= drag force	MLT^{-2}
g	= acceleration due to gravity	LT^{-2}
h	= distance from centre of sphere in vertical direction = $\sqrt{b^2 - a^2}$	L
k, k'	= integration constants	—
l	= distance in the direction of streamlines	L
n	= distance in the direction of equipressure lines	L
P	= pressure	$ML^{-1}T^{-2}$
R	= radius of cylinder of fluid round a particle	L
R_h	= half distance between particles in horizontal direction	L
r	= distance from centre of sphere in a horizontal direction	L
V	= relative velocity between fluid and particle	LT^{-1}
V_0	= terminal falling velocity	LT^{-1}
V_c	= falling velocity of suspension	LT^{-1}
β_e, β_t	= experimental and theoretical correction factors to Stokes' Law	—
ρ	= density of the liquid	ML^{-3}
ρ_s	= density of spheres	ML^{-3}
θ	= angle the streamlines make with the vertical	
γ	= is given by the relation $\beta_t = \frac{8}{9}\int_0^1 \gamma \frac{dh}{b}$	—
ϵ	= porosity	—

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[4] Richardson, J. F. and Zaki, W. N.; Trans. Inst. Chem. Eng. 1954.

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[6] Burgers, J. M.; Proc. K. Ned. Acad. Wet. 1942 45 126.

Book reviews

Rob Roy McGregor: Silicones and their Uses. McGraw-Hill Book Co., New York, 1954. pp. 302 + XV. Price $6.00.

This book is intended as a practical manual for engineers, metallurgists, chemists, etc. who intend to use silicones. There is little emphasis on the chemistry of the compounds, or on the reasons why silicones display such unusual properties, and non-chemical language is used wherever possible.

An excellent introductory account of the early history of silicon chemistry leads, *via* a note on the commercial development of silicones, to the second, and most useful, of the five chapters of the book. Over 150 pages are spent in describing the various types of silicones that can be obtained – silicone fluids, resins, lubricants, rubbers, etc. The physical properties and applications of these materials have been obtained mainly from industrial pamphlets etc. issued by several American companies, particularly the *Dow-Corning Corporation*. The information, which is neatly summarised and often tabulated, constitutes a very valuable compendium. The markedly non-critical approach is somewhat irksome, however, and there is a tendency to make silicones sound like a panacea for all ills.

The section on silicone fluids covers such topics as stability in air, resistance to heat or chemicals, effect on organic rubbers, solubility in various solvents, effects with metals, boiling and freezing point, viscosity and shear stability, lubricating and dielectric properties, water repellency, surface tension, specific heat, uses as anti-foaming agents, moulding, film, paper, textile additives, and hydraulic fluids. Occasional vague phrases of the type "continued exposure at high temperature" are encountered, but on the whole the information provided under each heading is adequate and often excellent.

Dimethyl silicones to which a few percent of a finely divided silica have been added have been termed "compounds," and the properties and uses of such materials, considered in the next short section of chapter 2, include antifoaming agents, tap greases, and electrical applications. This is followed by a surprisingly short section on silicone lubricants, and a particularly useful section on coating, laminating, release, water-repellant, moulding, and electrical resins. The following section on silicone rubber collects together for the first time information about chemical and physical properties (flexibility, hardness, tensile strength, elongation, compression set, chemical, oil, abrasion resistance, etc.), and includes a short account of the preparation and curing of the rubber.

A short chapter on the physiological effects of silicon compounds is used mainly to emphasise the inertness of silicones; it is followed by a chapter listing the uses of silicones in a variety of industries. The extent to which silicones are actually used as, say, "a defoamer for asphalt applied to highways" as compared with, say, "polishes for automobiles, furniture, and glass" is not indicated, and many of the "uses" listed would be more correctly classed as "suggestions." The last chapter, intended mainly for the non-chemist, gives a clear summary of the chemistry of silicon compounds and the methods used for the preparation of silicones.

The bibliography of 152 references is disappointingly small when one considers the vast number of papers which appear annually on the subject. The book is well set out and printed, has few factual or typographical mistakes, and has a good index. It is essentially a non-critical compilation of information and at times tends to read like a manufacturer's pamphlet. Nevertheless it fulfils a very useful purpose and is to quite an extent complementary to Rochow's *Introduction to the Chemistry of the Silicones*. It can be recommended to those likely to use or consider silicones as a means of solving specialised problems.

R. N. Haszeldine.

G. A. Morris and J. Jackson: Absorption Towers. Butterworths Scientific Publications, in association with Imperial Chemical Industries Limited, 1953. 159 pages. Price 30s.

This book is concerned primarily with the design of packed towers for the absorption or desorption of gases. The emphasis is on the methods and data needed by an engineer to design full-scale towers which are technically and economically satisfactory. The methods described are based largely on the results of work carried out by *Imperial Chemical Industries Limited*, much of which has previously not been published. Since the aim of the book is different from that of a text-book, the fundamental theories of diffusion and analogies between fluid friction, heat transfer, and mass transfer have been omitted, whereas considerable attention has been paid to economic factors and the design of liquid distribution systems.

Both absorption coefficients and transfer units are used in various illustrative examples. Simple types of laboratory absorption equipment, such as the falling-film tower and the disc tower, are considered first. These towers are then used as standards with which the performance of packed towers can be compared. Gas-film coefficients, for example, are estimated from data obtained in the falling-film tower, corrected by a gas-film packing factor. Liquid-film coefficients are estimated from data obtained in the standard disc tower, corrected by a liquid-film packing factor. These individual coefficients are combined in the usual way to give an overall coefficient which can be used for design. Individual and overall transfer units are estimated in a similar fashion. Systems in which absorption accompanied by chemical reaction occurs are discussed only very briefly.

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Several clearly worked examples are included to illustrate both the design of packed towers and the prediction of the performance of existing towers. There is a good discussion of wetting and flooding rates, pressure drop and economic gas rates for various packings. Several useful correlations and graphs are presented. Liquid and gas distribution systems are considered in detail.

This book should be most helpful as a reference work for design engineers. It is well written and contains much useful information. RAYMOND W. SOUTHWORTH.

Inorganic Syntheses. Volume IV. Editor-in-chief, J. C. BAILAR, JNR. McGraw-Hill Book Company, Inc., London. 1953. Price 36s.

The aim of *Inorganic Syntheses* is to provide in book form complete and independently tested directions for the laboratory preparation of a large number of important inorganic substances, most of which are not obtainable commercially. Each volume contains a selection of compounds of elements distributed throughout the periodic table ; the present volume includes lithium nitride, silver (II) oxide, calcium hydrogen phosphates, iodochlorosilanes, nitrosyl and nitryl chlorides, diethyl phosphite, sodium superoxide, addition compounds of chromium (VI) oxide, potassium ferrate, and several anhydrous metal halides. Cumulative subject and formula indexes cover Volumes I-IV and greatly facilitate search for information. On the experimental side this volume fully maintains the high standard of its predecessors ; some of the descriptions of properties, however (e.g., a very elementary account of the classification of halides) might well have been omitted in a book written mainly for research workers in inorganic chemistry. A. SHARPE.

C. K. INGOLD : **Structure and Mechanism in Organic Chemistry.** G. Bell & Sons Ltd., London, 1953. vii + 828 pp., 47 figures. Price £3. 17s. 6d.

This work is highly imposing and offers much more than an ordinary text-book. It presents a picture of the development of theoretical organic chemistry, which may be considered historically very valuable in view of the large contribution made to this development by the author. Besides, the book contains a wealth of information which, no doubt, will prove a great help to countless research chemists in studying their problems.

As a text-book for students of technology it is, undoubtedly, too exhaustive ; the advanced student specializing in organic chemistry, however, will find it a storehouse of knowledge.

In the initial chapters the author gives a clear picture of the development of the present structural formulation of organic compounds. Next he shows the reader how the modern theory is based on the physical study of matter and explains the terminology used in the following chapters.

In these chapters, as in the preceding ones, the matter discussed is amply illustrated with experimental data. Justly, a separate chapter has been devoted to the aromatic nucleus and the concept of the aromatic character. After this the author proceeds to give a classification of reagents and reactions.

The nucleophilic substitution is extensively discussed, which is not to be wondered at, in view of the large contribution to this field which has been made by Prof. INGOLD and his school.

In the last few years many books treating of theoretical organic chemistry have been published. In our opinion, however, the appearance of a work such as this, which, in its elaborateness, proves to be the fruit of many years of development, is a rare occurrence.

With gratitude we accept this book, which enables us to survey with the author, the achievements in this field of organic chemistry. Dr. G. DE JONG.

ROLAND S. YOUNG : **Industrial Inorganic Analysis.** London, Chapman and Hall Ltd., 1953. viii + 368 pages, 12 figs., 7 tables. Price 36s.

It has been the intention of the author – in view of, for example, the A.S.T.M. Methods of Chemical Analyses of Metals – to give a description of such methods of analysis as may occur in inorganic laboratory practice and which have not yet been described in full in any other book. It is a real pleasure to note that at long last there has appeared a book which, unlike practically all other analytical handbooks, does not start with 50-100 pages on general subjects which may well be considered as common knowledge.

Forty-four elements arranged in alphabetical order are discussed. For the determination and separation of each element, the author presents several methods supplemented with – on the whole – sound comments.

Whereas the methods given for the analysis of some elements (Cr, Ni) are very good, it must be remarked that several others seem to be rather obsolete. For example, the book contains quite a large number of determinations in which use is made of hydrogen sulphide, although, as is well known, the presence of H_2S in these tests is anything but desirable.

The chapter on Miscellaneous Analyses and Data, contains about 35 pages dealing with the determination of acids in some special samples, gas analyses, examination of water, examination of xanthates, standard acids and bases and indicators. Partly because of its conciseness, this appendix is much less successful than the part on the analysis of the elements.

The reference literature cited is chiefly by American authors. Much care has been given to the author and subject indexes.

Apart from a few inaccuracies, the book provides much useful information to the more experienced analytical chemist. H. W. DEINUM.

Letter to the Editors

Layer formation in a horizontal extractor

In an attempt to study mass transfer between two horizontal flowing viscous streams of carbontetrachloride with acetic acid as a solute and water, we met with the remarkable effect that no steady state conditions could be established even over very prolonged periods. The dimensions of the extractor used were 100 × 5 × 5 cm (length, width and height), the streams entered the apparatus without undue disturbance and ran countercurrently. At a volume rate of 3 l/hour for each stream, even after 16 hours, therefore after a passage of 38 times the volume of the apparatus, it appeared that the acetic acid content of the carbontetrachloride had decreased 20-30 % more than the increase in the acetic acid content of the water. The material balances were taken from the entering and leaving streams.

It turned out that this very slow establishment of steady state conditions is caused by a strong tendency for layer formation caused by density differences of solutions of different acetic acid content.

Proof is given by replacing during an extraction experiment the solutions of the otherwise same two liquids by coloured solutions of the same composition. It appeared that the colourless (upper) water layer was slowly replaced by the coloured water layer with the exception of a small zone just above the interface carbontetrachloride-water. For a volume rate of 3 l/hour of both streams at the entrance side of the water this uncoloured zone was 4 mm thick, at the exit side 7 mm, for hours. A very sharp separation between the two water layers existed. Apparently, just above the interface a more or less stagnant layer of higher density is formed, which accumulates part of the acetic acid passing the interface. This indeed could be shown with a universal indicator. Increasing the volume rate of the water stream was accompanied by a decrease in the thickness of the layer as could be expected. If a stream of a coloured 5 % brine solution of density 1·04 g/cm^3 was introduced after the experiment described above the very spectacular observation was made that the brine stream entered the colourless water layer like a wedge and split this colourless layer into two colourless layers. The layer near the interface of higher density than 1·04 g/cm^3 had a thickness of 1·5 mm.

For the carbontetrachloride stream the effect was the opposite, the coloured stream flowed along the interface. By a decrease in the acetic acid content, the density increases and in the direction of flow a mixing effect in a downward vertical direction was observed.

It is obvious that the effects described strongly will hinder mass transfer measurements in a horizontal apparatus. Although the influence of the concentration on the density is well known, the effect on the behaviour of a horizontal laminar flowing liquid is greater than we expected. Because this also might be the case with colleagues working in the same field, we thought it worth while to bring our observations to your notice.

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P. M. Heertjes
H. Talsma

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